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Carbon Capture, Utilization, and Storage (CCUS) and how to Accelerate the Development and Commercialization of Carbon Capture Technologies and Carbon-Based Products in the European and United States Markets

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SUMMARY

Global warming and climate change concerns have triggered international efforts to reduce the amount and concentration of CO_2 emissions to ward-off massive economic and environmental damages. In recent years, the development of efficient and cost-effective technologies for reducing anthropogenic CO_2 emissions have been gaining momentum all over the world.

The main subject of this work revolves around the CO_2 molecule, a low-value, low-energy, stable waste gas, often available in large quantity in single locations. This work examines some viable avenues to capture, utilize, and store CO_2 (CCUS)- with the ultimate goal of reducing GHGs emissions and global warming. Moreover, the study also examines various paths to accelerate the commercialization of the carbon-based products and their technologies.

Currently CCU technologies are experiencing various stages of performance and maturity; nonetheless, there are significant advancements in CCU technologies that have progressed in the past ten years; various technologies showing promising commercial scalability and advanced mobility features. Furthermore, the swift decline of costs for many renewable sources (mainly solar and wind) has made low-cost, near-zero-carbon electricity abundant in terms of capacity and locality. Consequently, this has driven some markets to offer electricity at affordable cost and, in some cases even negative prices. Because renewable electricity is gradually decreasing in price, there has been an increase cognizance on prospective new applications, (e.g., CCU and CCUS) considering turning this trend into a profitable venture.

This work focuses on six major aspects related to emerging renewable energy based CCUS processes and technologies:

1. A thorough investigation of three emerging renewable energy technologies and processes (RETP) (i.e., biogas & fuel cells, synthetic fuels, mineral carbonation of fly ashes) that fall into the CCUS paradigm and are either special, relatively new, or advanced forms of the mainstream energy sources. Each RETP CCUS's explanation is followed by its market share, challenges, implications for increased adoption, prospects, and drawbacks.
2. Analysis of experimental work related to the direct use of CO_2-containing fuel of biological origins to supply an electrochemical process devoted to the production of power at high efficiency. Furthermore, the work analyzes a case study called DEMOSOFC located at a wastewater treatment plant (WWTP) in Torino, Italy. It looks at the production of energy by utilizing biogas produced at WWTPs and reports findings of the use of Carbon (contained in CO_2) as it is to produce power and heat (in CHP configuration) using fuel cells; specifically, solid oxide fuel cells.
3. Analysis of experimental and modeling work done at Politecnico di Torino linked to the use of the Carbon molecule to produce synthetic fuels (e-methane (CH_4) and e-methanol (CH_3OH)) by means of two processes: steam electrolysis + methanation, and steam electrolysis + methanol production.

4. Analysis of the chemical process called mineral carbonation (MC), a carbon capture utilization and storage (CCUS) technology that can capture large quantities of CO_2 and convert it into stable carbonate products that can easily be used in the cement and concrete market. The work brings forward pragmatic evidence that MC production has the potential to deliver net positive revenue and its commercial feasibility is a realistic venture. However, the prospective of a new direction of cementation by the carbonation of FA is still maturing but with great potential for accelerated commercialization. The intensification of environmental and economic benefits generated by this new pathway for cementation are substantial if compared to the current methods of using FA in the construction industry. Yet, existing carbon policies and regulations, restricting the use of fly ashes (mainly those ashes containing larger quantities of calcium-HCFA) can impact the progress of carbon capture technologies and the commercialization of carbon-based products.

5. The examination of the potential commercialization of CCUS technologies by identifying four major markets and eight product categories critical to driving further investments and innovation at an accelerated pace. Funding and incentives are necessary for most of these products to accelerate development and achieve full-scale commercial roll out capability. The major markets and product discussed in this chapter are: (1) Markets- Building materials, chemical intermediates, fuels, polymers (2) Products- carbonate aggregates, methanol, formic acid, syngas, liquid fuels, methane, polyols and polycarbonates.

6. It assesses the continuing increase in RETP CCUS despite the Covid-19 pandemic resulting from a mixture of past policies, regulations, incentives, and innovations embedded in the power sectors of many forward-thinking countries. Furthermore, it looks at the future of RETP CCUS post-pandemic period.

SOMMARIO

Le preoccupazioni per il riscaldamento globale e il cambiamento climatico hanno innescato gli sforzi internazionali per ridurre la quantità e la concentrazione delle emissioni di CO_2 per scongiurare enormi danni economici e ambientali. Negli ultimi anni, lo sviluppo di tecnologie efficienti e convenienti per ridurre le emissioni di CO_2 antropogeniche ha preso piede in tutto il mondo.

L'argomento principale di questo lavoro ruota intorno alla molecola di CO_2, un gas di scarto a basso valore, a bassa energia e stabile, spesso disponibile in grandi quantità in singole località. Questo lavoro esamina alcune strade percorribili per catturare, utilizzare e immagazzinare la CO_2 (CCUS), con l'obiettivo finale di ridurre le emissioni di gas serra e il riscaldamento globale. Inoltre, lo studio esamina anche vari percorsi per accelerare la commercializzazione dei prodotti a base di carbonio e delle loro tecnologie.

Attualmente le tecnologie CCU stanno vivendo vari stadi di performance e maturità; tuttavia, ci sono progressi significativi nelle tecnologie CCU che hanno progredito negli ultimi dieci anni; varie tecnologie che mostrano una promettente scalabilità commerciale e caratteristiche di mobilità avanzate. Inoltre, il rapido declino dei costi di molte fonti rinnovabili (principalmente solare ed eolico) ha reso l'elettricità a basso costo e quasi a zero emissioni di carbonio abbondante in termini di capacità e località. Di conseguenza, questo ha spinto alcuni mercati a offrire elettricità a costi accessibili e, in alcuni casi, anche a prezzi negativi. Poiché l'elettricità rinnovabile sta gradualmente diminuendo di prezzo, c'è stato un aumento della conoscenza delle nuove applicazioni potenziali, (per esempio, CCU e CCUS) considerando di trasformare questa tendenza in un'impresa redditizia.

Questo lavoro si concentra su sei aspetti principali relativi ai processi e alle tecnologie emergenti di CCUS basati sull'energia rinnovabile:

1. Un'indagine approfondita di tre tecnologie e processi emergenti di energia rinnovabile (RETP) (cioè, biogas e celle a combustibile, combustibili sintetici, carbonatazione minerale di ceneri volanti) che rientrano nel paradigma CCUS e sono speciali, relativamente nuovi, o forme avanzate delle fonti di energia tradizionali. La spiegazione di ogni RETP CCUS è seguita dalla sua quota di mercato, dalle sfide, dalle implicazioni per una maggiore adozione, dalle prospettive e dagli svantaggi.
2. Analisi del lavoro sperimentale relativo all'uso diretto del combustibile contenente CO_2 di origine biologica per alimentare un processo elettrochimico dedicato alla produzione di energia ad alta efficienza. Inoltre, il lavoro analizza un caso di studio chiamato DEMOSOFC situato in un impianto di trattamento delle acque reflue (WWTP) a Torino, Italia. Esso esamina la produzione di energia utilizzando il biogas prodotto presso il WWTP e riporta i risultati dell'uso del carbonio (contenuto nella CO_2) per produrre energia e calore (in configurazione CHP) utilizzando celle a combustibile; in particolare, celle a combustibile a ossido solido.

3. Analisi del lavoro sperimentale e modellistico svolto presso il Politecnico di Torino legato all'utilizzo della molecola del Carbonio per produrre combustibili sintetici (e-metano (CH_4) ed e-metanolo (CH_3OH)) attraverso due processi: elettrolisi a vapore + metanazione, ed elettrolisi a vapore + produzione di metanolo.

4. Analisi del processo chimico chiamato carbonatazione minerale (MC), una tecnologia di cattura, utilizzo e stoccaggio del carbonio (CCUS) che può catturare grandi quantità di CO_2 e convertirla in prodotti carbonati stabili che possono essere facilmente utilizzati nel mercato del cemento e del calcestruzzo. Il lavoro porta avanti la prova pragmatica che la produzione MC ha il potenziale per fornire un reddito netto positivo e la sua fattibilità commerciale è un'impresa realistica. Tuttavia, la prospettiva di una nuova direzione di cementazione tramite la carbonatazione di FA è ancora in fase di maturazione ma con un grande potenziale di commercializzazione accelerata. L'intensificazione dei benefici ambientali ed economici generati da questo nuovo percorso per la cementazione sono sostanziali se paragonati agli attuali metodi di utilizzo dell'AF nell'industria delle costruzioni. Tuttavia, le politiche e i regolamenti esistenti sul carbonio, che limitano l'uso delle ceneri volanti (principalmente quelle ceneri che contengono maggiori quantità di calcio-HCFA) possono avere un impatto sul progresso delle tecnologie di cattura del carbonio e sulla commercializzazione dei prodotti a base di carbonio.

5. L'esame della potenziale commercializzazione delle tecnologie CCUS identificando quattro mercati principali e otto categorie di prodotti critici per guidare ulteriori investimenti e innovazione ad un ritmo accelerato. I finanziamenti e gli incentivi sono necessari per la maggior parte di questi prodotti per accelerare lo sviluppo e raggiungere una capacità di lancio commerciale su larga scala. I principali mercati e prodotti discussi in questo capitolo sono: (1) Mercati - materiali da costruzione, intermedi chimici, combustibili, polimeri (2) Prodotti - aggregati carbonati, metanolo, acido formico, syngas, combustibili liquidi, metano, polioli e policarbonati.

6. Valuta il continuo aumento di RETP CCUS nonostante la pandemia di Covid-19 derivante da una miscela di politiche passate, regolamenti, incentivi e innovazioni incorporati nei settori energetici di molti paesi lungimiranti. Inoltre, guarda al futuro di RETP CCUS dopo la pandemia.

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1. EU-SPRI2019: The changing entrepreneurial finance landscape: challenges for policy conference- September 24-25, 2019; Turin, IT. Extended abstract for submission: “Carbon capture utilization and storage (CCUS) and the effects financial markets, regulatory framework, and policy changes have in the commercial acceleration of carbon-based products in the concrete/construction industry in the U.S. and European markets.

2. IRMBAM: International Research Meeting in Business and Management- April 2017. Paper submitted: “Analysis of waste treatment sector as a driver for SOFC cost reduction and commercialization”.

3. ISEFI: International Symposium on Environmental and Energy Finance Issues- March 2017. Paper submitted: “Analysis of waste treatment sector as a driver for SOFC cost reduction and commercialization”

4. InnoEnergy Iberdrola Challenge 2017. Paper submitted: “From sludge to energy: the nexus between renewable energy technologies and decentralized wastewater treatment facilities for the sustainable development of third-world countries”

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LIST OF ACRONYMS, PARAMETERS AND SUBSCRIPTS

Acronyms

CHP	Combined heat and power
EL	Electrolyzer
EMS	Energy management strategy
EPS	Electro Power System
EU	European Union
FC	Fuel cell
GDP	Gross domestic product
GHG	Greenhouse gas
G2P	Gas to power
LCOE	Levelized cost of energy
LF	Load factor
LHV	Lower heating value
NPC	Net present cost
OM	Operation and maintenance
PEMFC	PEM fuel cell
PV	Photovoltaic
P2C	Power-to-chemicals
P2G	Power-to-gas
P2L	Power-to-liquid
P2X	Power-to-X
RES	Renewable energy source
WT	Wind turbine
XRD	X-Ray powder diffraction

Parameters

A	heat exchange area (m2)
BEC	bare erected cost ($)
C	cost ($ MWh-1) or ($ kg-1)
CF	Cash flow ($)
Cp	purchasing equipment cost for components operating at base conditions ($)
DA	gas diffusivity (m2 s-1)
De	diffusion coefficient (m2 s-1)
Dep	depreciation

Dp	diameter of the catalyst particle (m)
E	chemical energy (MWh)
EPCC	engineering, procurement and construction cost ($)
Exp	operating expenses ($)
f	cost scaling factor
FM	Material factor
Fp	Pressure factor
h	molar enthalpy (J mol-1)
k’	ratio between the rate constant calculated with the LHHW expression and the concentration of the reactant in the catalyst volume (s-1)
LHV	lower heating value (J kg-1)
$\dot{n}$	molar flow rate (mol s-1)
NPV	net present value ($)
Rev	operating revenues ($)
rt	tax rate
S	equipment cost attribute
TOC	total overnight capital ($)
TPC	total plant cost ($)
Tx	taxes ($)
U	global heat transfer coefficient (kW m-2 K-1)
UF	utilization factor
W	power (W)
ΔTml	logarithmic mean temperature difference (K)
η	efficiency
τi	Tortuosity coefficient
φ	Thiele modulus
Φ	heat flow rate (kW)

Subscripts

0	base conditions

an	anode
cat	cathode
compr	compression
el	electrical
in	inlet
LT	lifetime
min	minimum
n	reference year
out	outlet
PP	pinch point
prod	product

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Introduction and Overview

The world is entering an era where renewables will make up an increasing share of our electricity supply; moreover, this electricity stock will extend to other energy forms and the production of carbon-based commodities. Effective shifts of global energy systems could well foster wide-ranging economic growth, energy efficiency and affordability, and energy supply security. However, despite the enormous efforts to mitigate environmental depredation, it is sorely evident that we are extremely far to meet the targets for preventing temperature rise of 1.5°C to which nearly all nations have agreed [1].

According to Our World in Data journal, the global average temperatures have increased by more than 1℃ since pre-industrial times (Fig. 1). The global average temperature rise is usually given as the combined temperature change across both land and the sea surface. However, it is important to note that land areas change temperature, both warming and cooling much more than oceanic areas. Overall, global average temperatures over land have increased around twice as much as the ocean [2].

Furthermore, the Northern Hemisphere has more mass, therefore, the change in average temperature north of the equator has been higher than the Southern Hemisphere. Finally, there are some regions in the world where temperatures can be more extreme. At very high latitudes, especially near the Poles, warming has been upwards of 3°C, and in some cases exceeding 5°C. These are, unfortunately, often the regions that could experience the largest impacts such as sea ice, permafrost, and glacial melt. Monitoring the average global temperature

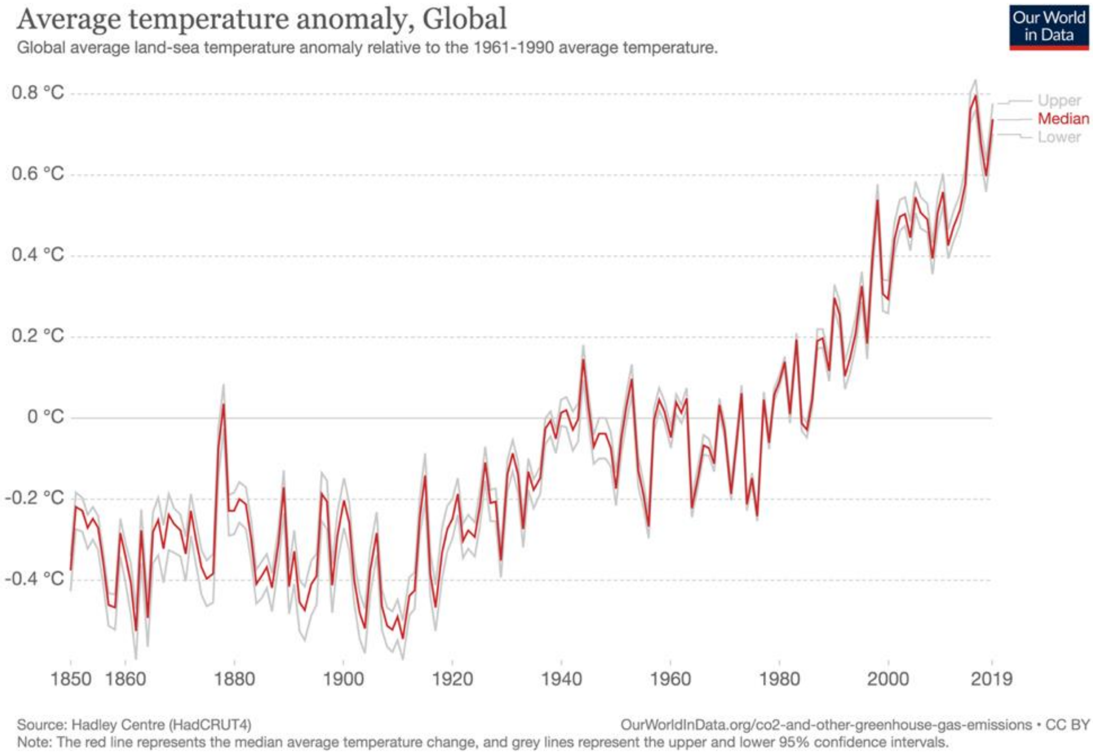


Fig. 1.Global average temperature anomaly [3]

Multiple gases contribute to the greenhouse effect that sets Earth's temperature over geologic time. However, the three main GHGs responsible for a large portion of recent global warming are: CO_2, CH_4, N_2O (Table 1) [4].

Table 1. Atmospheric lifetime and Sources of three major GHG's [5]

Greenhouse gas	Chemical formula	Atmospheric lifetime-yrs.	Major Sources
Carbon Dioxide	CO_2	100	Fossil fuel combustion; Deforestation; Cement production
Methane	CH_4	12	Fossil fuel production; Agriculture; Landfills
Nitrous Oxide	N_2O	121	Fertilizer application; Fossil fuel and biomass combustion; Industrial processes

This work will mainly focus on the GHG of CO_2 and three processes related to CCUS. Figure 2 shows the growth of global emissions from the mid-18th century up to 2019. It can be observed that prior to the Industrial Revolution emissions of CO_2 were relatively low. In 1950 the world emitted just over 5 billion tons of CO_2; by 1990 this discharge had quadrupled to 22 billion tons. Emissions have continued to grow rapidly; today the world emits over 36 billion tons each year [3]. Emissions growth has slowed over the last few years, but they have yet to reach their peak.

Most of the CO_2 emissions is due to the combustion of fossil fuel and industrial processes in order to generate electricity and heat (Fig. 3) [6]. Additionally, other industrial processes related to the production to steel, cement, and some chemicals play a significant role in the emissions of GHGs.

Global GHGs emissions can also be broken down by a range of sectors and processes. The overall picture demonstrates that almost three-quarters of emissions come from energy use; almost one-fifth from agriculture and land use; and the remaining 8% from industry an waste (Fig. 4) [3].

Lastly, Figure 5 shows the production of CO_2 (i.e., production-based CO_2 not where is finally consumed) by country. The three major emitters are Asia, North America, and Europe. Asia is by far the largest emitter, accounting for 53% of global emissions (based on 2017 data), approximately 10 billion tons each year, more than one-quarter of global emissions. North America- dominated by the U.S.- is the second largest regional emitter at 18% of global emissions; followed closely by Europe (EU-28) with 17% [3].

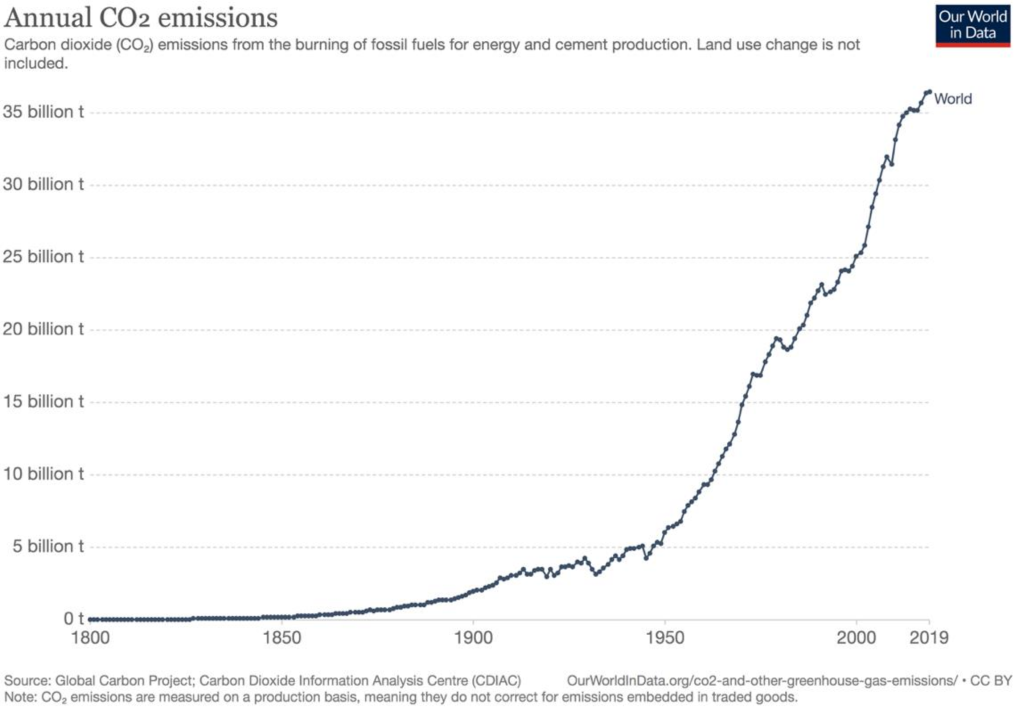


Fig. 2. Annual CO_2 emissions growth [3]

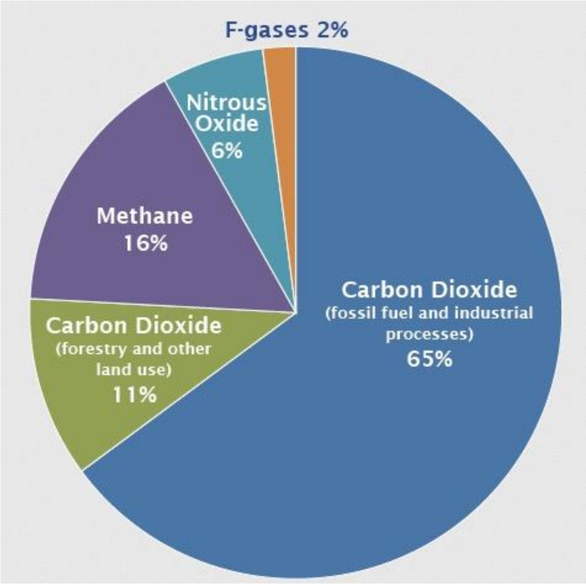
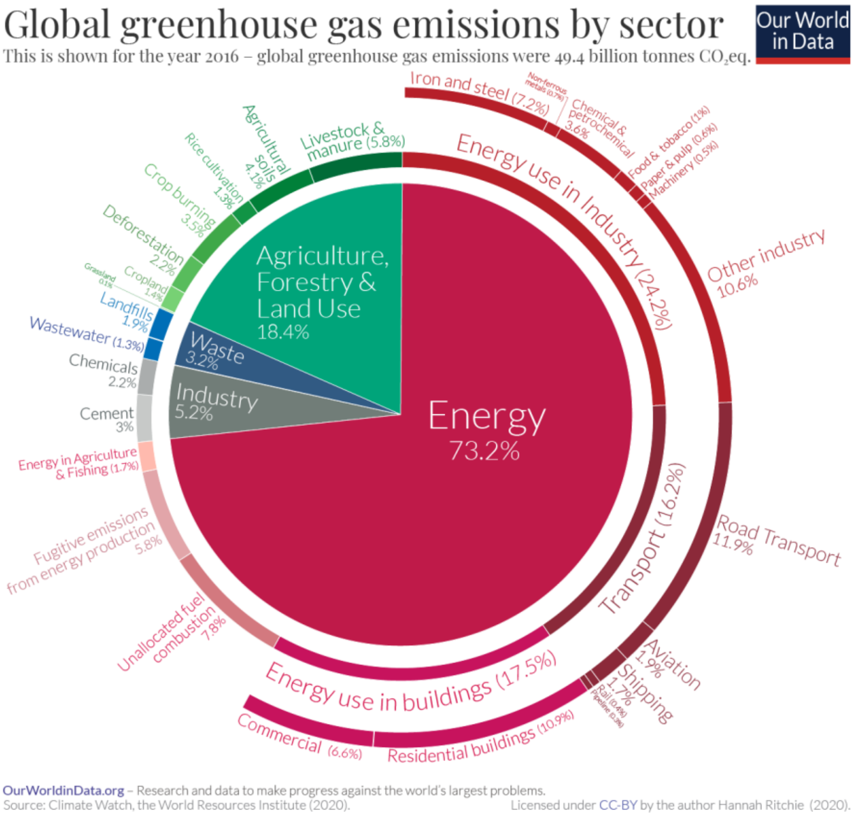


Fig. 3. Global GHG Emissions by Gas [6]


Global greenhouse gas emissions by sector

This is shown for the year 2016 – global greenhouse gas emissions were 49.4 billion tonnes CO_2eq.

OurWorldinData.org – Research and data to make progress against the world's largest problems.
Source: Climate Watch, the World Resources Institute (2020).

Fig. 4. Where do GHG global emissions come from-2016 [3]

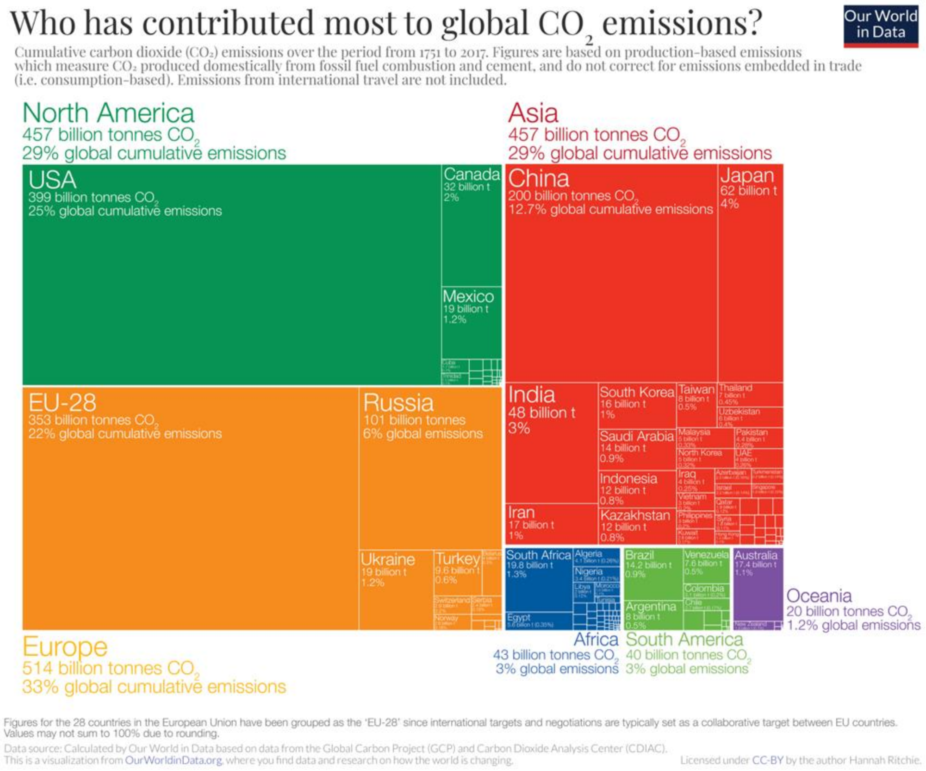


Fig. 5. Where do GHG global emissions come from-2017 [3]

CCUS is an appealing approach to combat global warming not only because of its prospective for emissions curtailment but also because it allows for the creation of valuable commodities such as fuels, construction materials, plastics, and other useful products.

There are different commercial technologies to capture CO_2 from a stationary source (e.g., coal-fired power plants). The CCUS process usually involves CO_2 separation (either from the flue gas or other intermediate streams) followed by pressurization, transportation, and sequestration. According to the International Energy Agency's roadmap, 20% of the total CO_2 emissions should be removed by CCUS by year 2050 [7].

There are three categories of CO_2 capture systems that could be used at power stations and industrial emitters: post-combustion, pre-combustion and oxy-firing (Fig. 6) [8].

In post-combustion capture, CO_2 is separated from the flue gas after the combustion of fossil fuel. This process can be added, or retro-fitted, to existing power stations, either coal or natural gas-fired.

During pre-combustion capture the fossil fuel is reacted with steam and oxygen, producing a synthetic gas (syngas) which is made up of mostly carbon monoxide (CO), carbon dioxide, and hydrogen (H_2). An additional reaction with water (known as a water gas shift) can be used to convert the residual carbon monoxide to CO_2 and additional hydrogen. The CO_2 is removed, and the H_2 can then be combusted or oxidized electrochemically to produce electricity [9].

Oxy-firing combustion capture includes the combustion of fuel (coal or gas) in pure oxygen or oxygen-enriched air. The process can produce about 75% less flue gas than air-fueled combustion and the exhaust consists of between 80-90% CO_2. The remaining gas is water vapor, which simplifies the CO_2 separation step. An air separation plant is required to produce pure oxygen for the process from air.

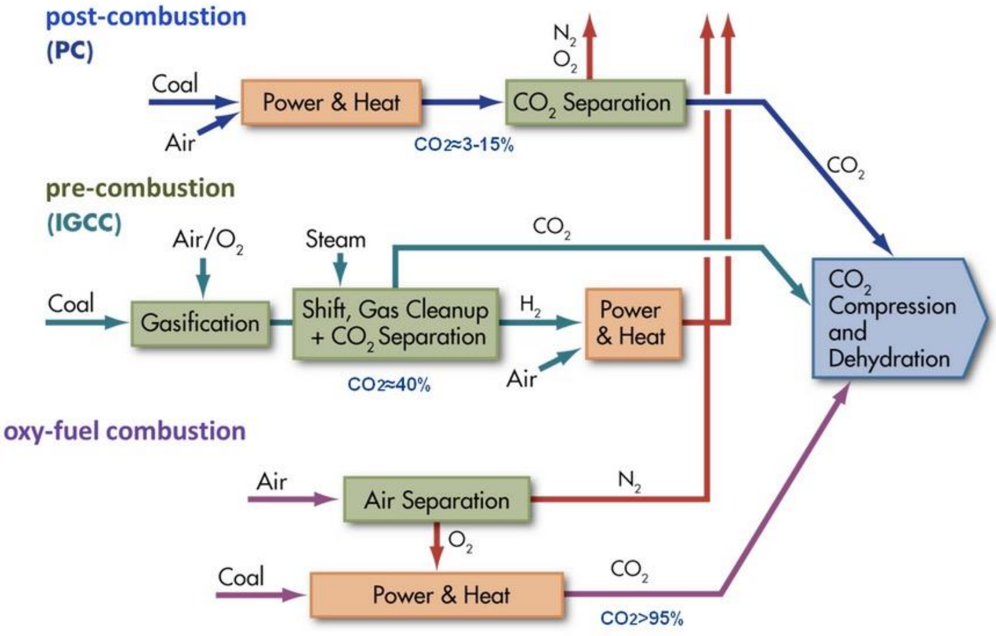
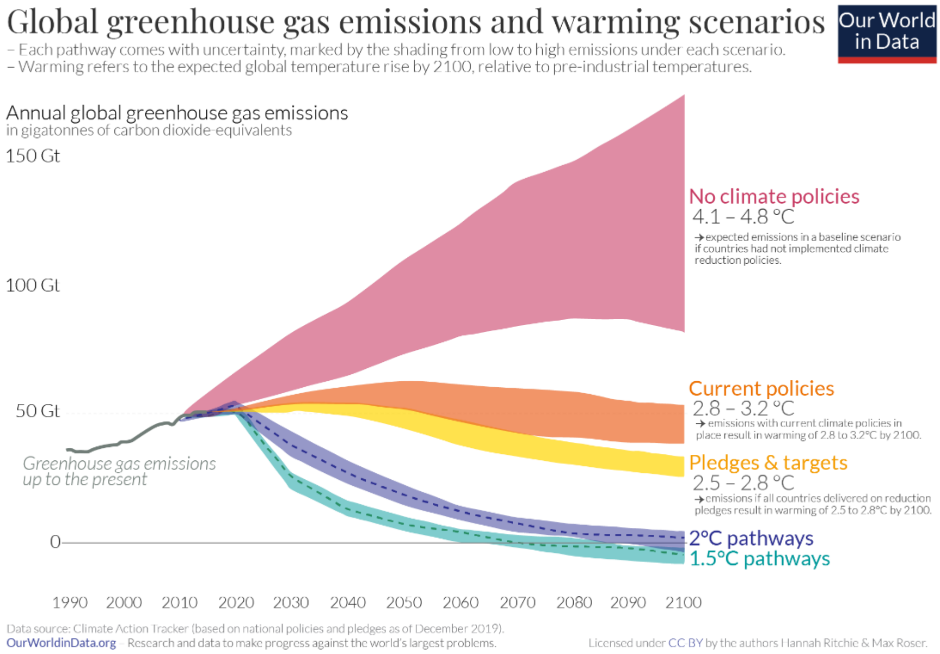


Fig. 6. Summary of CO2 capture technologies [8]

Cutting carbon emissions takes smart policies, innovative technologies, business leadership, and simple steps to shrink our own carbon footprint [4]. As depicted in Figure 7, current climate and energy policies could decrease global warming relative to a world with no climate policies in place. It can also be observed, future GHG emissions states under a variety of assumptions: (1) no climate policies; (2) current policies continue to be implemented; (3) if all countries realized their current and future pledges and targets to reduce GHG emissions; (4) follow the crucial pathways that are fitting with curbing global warming to 1.5°C or 2°C [10].


Global greenhouse gas emissions and warming scenarios

– Each pathway comes with uncertainty, marked by the shading from low to high emissions under each scenario.
– Warming refers to the expected global temperature rise by 2100, relative to pre-industrial temperatures.

Data source: Climate Action Tracker (based on national policies and pledges as of December 2019).
OurWorldinData.org – Research and data to make progress against the world's largest problems.
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Fig. 7. Climate policies will reduce GHG emissions, but not quickly enough to reach global targets [3]

1.1 The CCU Market

CCUS is a noteworthy path towards remediating global warming, especially in the short-to-medium term, during a complete transition to decarbonization. Moreover, it allows for the creation of valuable commodities based on the Carbon atom.

A comprehensive market assessment study finalized in 2016 by the Global CO_2 Initiative (GCI), presents a roadmap for potential commercialization of CCU technologies through 2030. The work identified four major markets and eight product categories critical to driving further investments and innovation at an accelerated pace. Funding and incentives are necessary for most of these products to accelerate development and achieve full-scale commercial roll out capability [11].

- Building materials or Concrete
    - Carbonate aggregates
- Chemical Intermediates
    - Methanol
- Formic acid
    - Syngas
- Fuels
    - Liquid fuels
    - Methane
- Polymers (polyols and polycarbonates)

The National Energy Technology Laboratory (NETL) research revealed that noteworthy advancement in carbon capture and utilization (CCU) and carbon capture, utilization, and storage (CCUS) has been made in the past ten years, with many technologies demonstrating to be scalable [12].

According to GCI the market size and CO_2 reduction potential can be significantly impacted by taking action now. Figure 8 below demonstrates the potential CO_2 reduction due to implementing strategic key actions from five markets. For example, the fuel market can increase the CO_2 reduction by 15-fold (from 0.03 b tons to 0.5b tons). Moreover, the market for CO_2-based fuels can be quadrupled by 2025 (from \$50b to \$200b) (Fig. 9) [11].

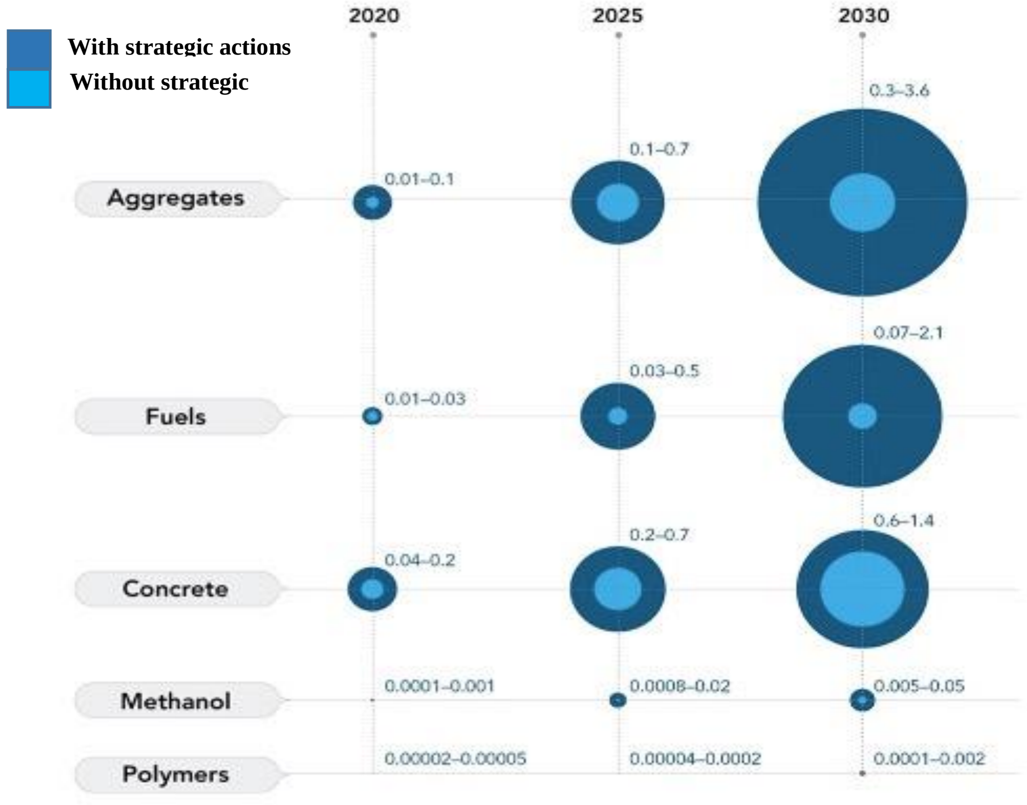


Fig. 8. Potential CO_2 reduction of CO_2 emission due to implementing strategic actions key [11]

According to GCI the recommended strategic actions to meet climate goals and accelerate commercialization of carbon-based products are [11]:

- Technology: fund applied research on technologies and applications that have the highest CO_2 abatement potential.
- Market: make funding available to established collaborations among research institutes, start-ups, governments and corporations for process integration of CO_2 conversion, hydrogen generation and carbon capture.

- Policy: supportive policies can help start and build markets for CO_2U products.

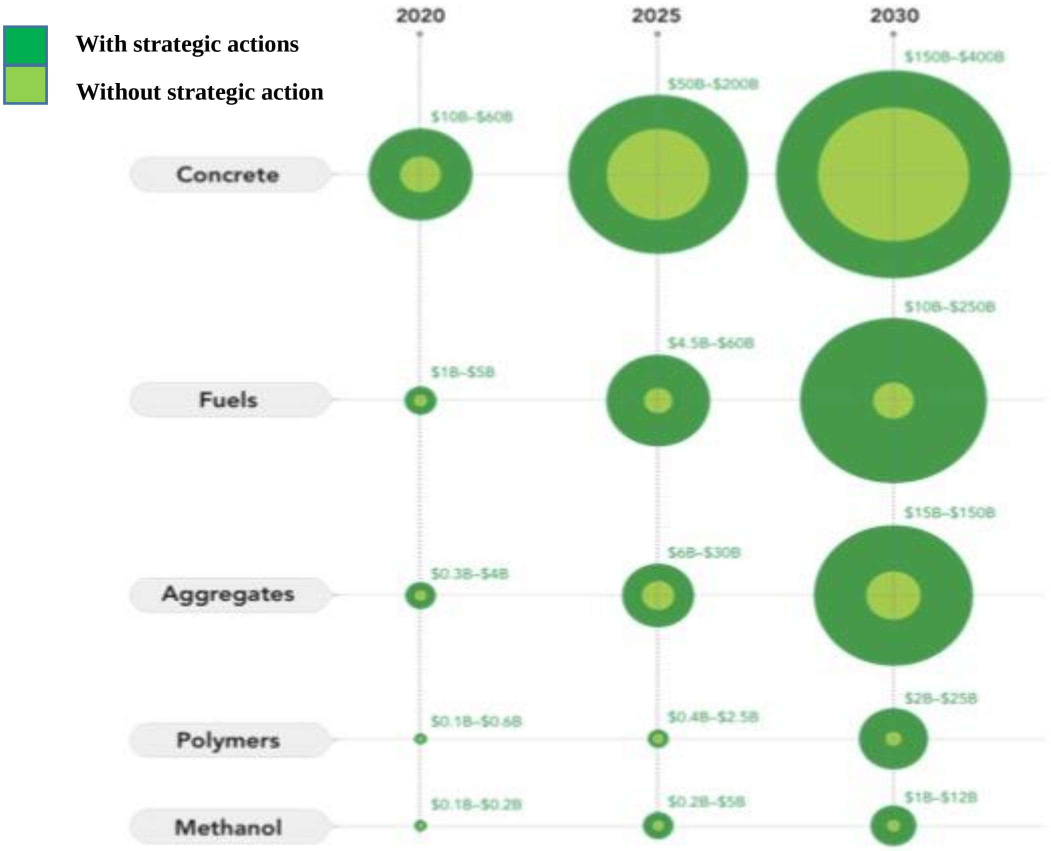


Fig. 9. Potential increase in market size due to implementation of strategic actions key [11]

At full scale, five CO_2U products could create a market over US$800 billion by 2030. CO_2U has the potential of utilizing 7 billion metric tons of CO_2 per year by 2030- the equivalent of approximately 15% of current annual global CO_2 emissions [11].

1.2 Renewable energy technologies, their market, and the Covid19 pandemic

Nearly every international climate change scenario under the 2015 Paris Agreement shows the need for a vast ramp-up in CCUS technologies to meet global targets. Timing matters, not just scale.

CCUS technologies must be deployed at scale swiftly if the Paris Agreement's objective of holding the increase in the global average temperature to well below 2℃ above pre-industrial levels is to be attained [13].

Prior to the recent Covid-19 pandemic, the enactment of the rules for the Paris Agreement were expected to be finalized in 2020 [13]. However, due to the global pandemic the 26th Conference of the Parties was rescheduled for November 2021 in Glasgow, Scotland [14].

The Covid-19 crisis has caused people to have limited social freedom, massive loss of jobs, and worldwide deaths. On the other hand, it has led to a decline in domestic waste because people who are quarantined for long periods of time are fearful of waste due to their sociological distresses. Moreover, the decrease of GHG emissions has significantly declined due to the abridged use of major means of transportation, the reduction of industrial operations, and the educational and social constraints. However, these changes in paradigm have not been enough to curtail air pollution and the damaging escalation of global warming.

Despite all the worldwide challenges the pandemic has caused, the growth in renewable has not diminished. In 2021, renewables are expected to show their resilience; the majority of the delayed projects are expected to come online, leading to a rebound in new installations [15]. As a result, 2021 is forecast to reach the same level of renewable electricity capacity additions as in 2019. Despite the rebound, combined growth in 2020 and 2021 is almost 10% lower compared to the previous IEA forecast published in October 2019 [16].

Covid-19 has brought the generation of energy from fossil fuels to breaking point. As the lockdown measures were introduced, global energy demand dropped precipitously at levels not seen in 70 years [15]. The IEA estimated that overall energy demand contracted by 6% and energy-related emissions decrease by 8% for 2020. Moreover, projections estimated a drop in oil demand of approximately 9% and coal 8% while crude oil is at record-low prices [16].

With the fall in demand, renewable sources (mainly wind and solar) saw their share in electricity substantially increase at record levels in many countries [17]. In less than 10 weeks, the U.S. increased its renewable energy consumption by nearly 40% and India by 45%; Italy, Germany, and Spain set new records for variable renewable energy integration to the grid (Fig. 10) [15]. However, the renewable energy market has experienced a downfall due to problems such as delays in the supply chain, problems in tax stock markets, and the risk of not being able to benefit from government incentives ending in 2020 [18] and most likely in 2021 as well

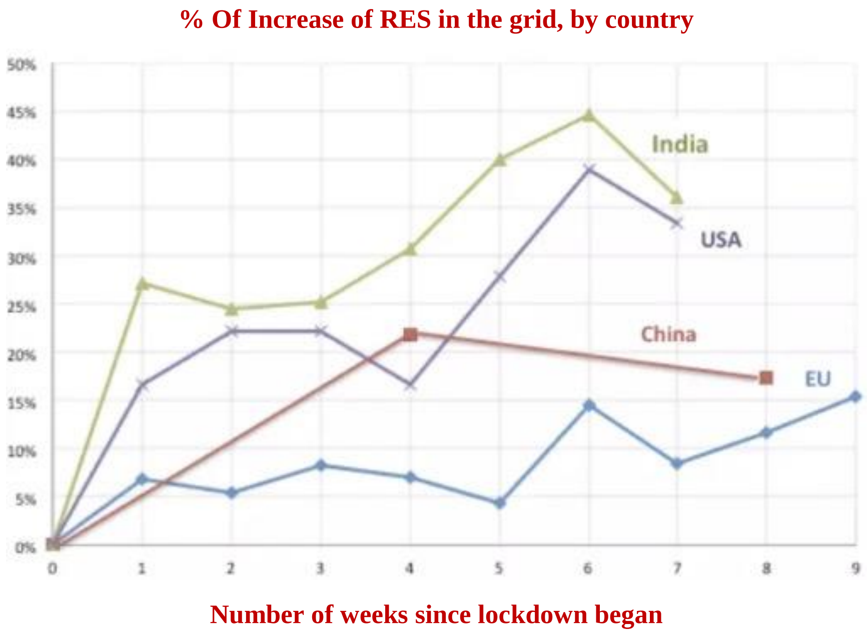


Fig. 10. Across the world, Renewable Energy demand jumped after the Covid-19 Lockdown, [15]

Although the pandemic is circumstantial and unexpected, the current outcome for the power sector is not. The continuing increase in renewable energy into the grid results from a mixture of past policies, regulations, incentives, and innovations embedded in the power sectors of many forward-thinking countries [15].

These are three key factors behind the increase in renewable energy during this crisis:

1. **Renewables have been supported by favorable policies**. In many countries, renewables receive priority through market regulation. The priority for the first batch of energy to the network is given to the less expensive source, favoring cheaper and cleaner sources.

2. **Continuous innovation.** Renewable energy has become the cheapest source of energy. IRENA recently reported that the cost of solar had fallen by 82% over the last 10 years [19], while Bloomberg New Energy Finance (BNEF) states that renewable energy is now the cheapest energy source in two-thirds of the world [20].

3. **Preferred investment.** Renewable energy has become investors' preferred choice for new power plants. For nearly two decades, renewable energy capacity has grown steadily, and now 72% of all new power capacity is a renewable plant [21].

As businesses, industry, and households focus on resuming their operations, the lockdown offers a real sense of opportunity for the energy sector. It creates plenty of lessons about clean energy policy, changes in demand patterns, and knowledge for a greener grid without compromising the security of supply. It also begins further opportunities for investment and innovation [15] . Imperial College reported on June 2020, that renewable power shares offer investors not only higher total returns relative to fossil fuels but also lower annualized volatility [22].

As governments begin to structure new regulations and support businesses for the post-Covid-19 world, they are drawing up stimulus plans in an effort to counter the economic damage from the coronavirus and secure greater investment to become more competitive. These stimulus packages offer excellent opportunities [18] to ensure that crucial tasks of building a safe and sustainable energy future does not get lost among the flurry of immediate priorities.

Large-scale investment to boost the development, deployment and incorporation of clean energy technologies (e.g., solar, wind, hydrogen, batteries, CCUS) needs to be an essential part of governments' plans because it will bring the dual benefits of stimulating economies and accelerating clean energy transitions [18]. Strong political backing can provide clear policies and long-term plans, governments can reduce the uncertainty that is holding back investors and business from channeling far more money into sectors like renewables [23].

The coronavirus crisis is already doing substantial damage around the world. Rather than compounding the tragedy by allowing it to hinder clean energy transitions, we need to seize the opportunity to help accelerate them. At the heart of the matter is energy [7], which is responsible for more than two-thirds of global greenhouse gas emissions [4]. To put the world firmly on track to meet international climate goals, the industry and governments need to take action to make sure those emissions peak as soon as possible and then put the effort toward driving them into a steep decline [23].

1.3 Biogas production and utilization at full-scale wastewater treatment plant

"Biogas" is a gas produced by anaerobic fermentation of different forms of organic matter and is composed mainly of CH_4 and CO_2 (Fig. 11). With little to no processing, biogas can be burned on-site to heat buildings and power boilers. Biogas can be used for combined heat and power (CHP) operations, or biogas can simply be turned into electricity using a combustion engine, fuel cell, or gas turbine, with the resulting electricity being used on-site or sold onto the electric grid [24].

Biogas systems turn the cost of waste management into a revenue opportunity [25]. Converting waste into electricity, heat, or vehicle fuel provides a renewable source of energy that can reduce dependence on foreign oil imports, reduce GHG emissions, improve environmental quality, and increase local jobs [24].

The U.S. has over 2,200 sites producing biogas: 191 anaerobic digesters on farms, approximately 1,500 anaerobic digesters at wastewater treatment plants (only 250 currently use the biogas they produce)

and 576 landfill gas projects. By comparison, Europe has over 10,000 operating digesters; some communities are essentially fossil fuel free because of them [26].

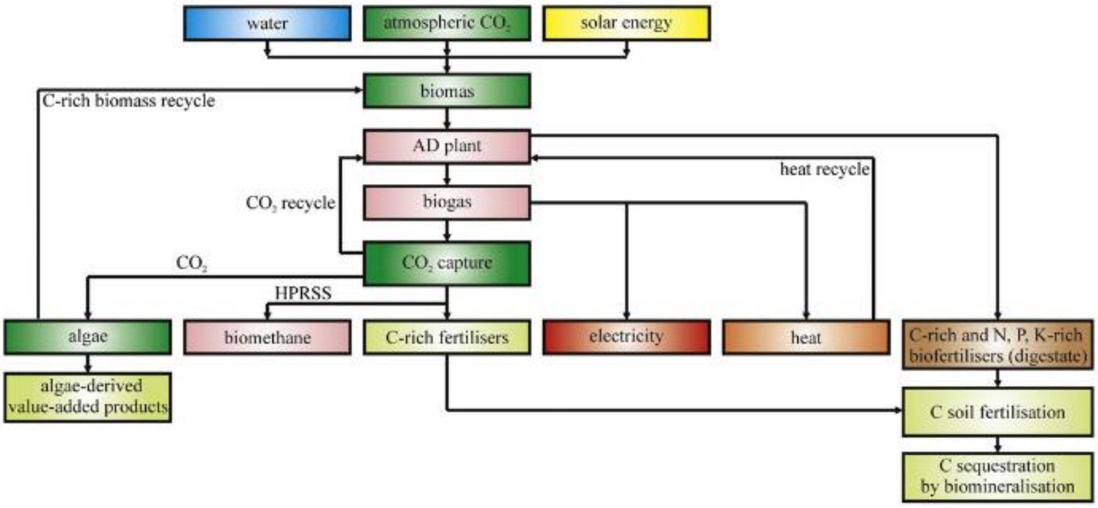


Fig. 11. Value-added anaerobic digestion of biomass-to-biogas, biomethane, electricity, C-rich and fertilizers and algae-derived value-added products [27]

Different studies have focused on solutions to increase the energy efficiency of WWTPs. The goal of having WWTPs as net energy producers is an ambitious yet feasible one [28] [29]. The self-sufficiency target is deemed an achievable one since wastewater already contains two to four times the amount of energy needed for the wastewater treatment process [30].

Reducing energy consumption and increasing the efficiency of energy production are both required to have positive energy WWTPs. Measures to reach self-sufficient WWTPs are listed below [31].

- Process optimization: this approach consists in installing smart meters [32] within the plant and developing control systems for the optimal operation of aeration systems and water pumps (aeration is part of the secondary biological treatment, which takes more than 50% of the overall electrical consumption [33] [34]). EPRI has estimated that, in wastewater facilities, 10-20% energy savings are possible through better process control and optimization [35].
- Enhanced biogas yield: currently, anaerobic digestion (AD) biogas can only provide around 50% of the total energy consumption [36]. However, sludge pre-treatments [30] can lead to an increase of the biomethane yield.
- Efficient on-site combined power and heat (CHP) generation: the use of fuel cell systems (e.g., SOFC plants) can increase further the on-site electricity generation, which is key to self-sufficiency.
- Co-digestion of sludge with food waste is also an interesting option to increase the overall biogas output.

Self-sufficiency has been already achieved, for example, in the Strass im Zillertal Wastewater Treatment Plant in Austria [37]. Here, thanks to sludge pre-thickening systems, improvement of the aeration system, development of an innovative nitrogen removal equipment and increasing the CHP efficiency, energy self-sufficiency has been reached already in 2005 [37] when the onsite production overtook electrical consumption.

In this context, the use of the CO_2 compound contained in the biogas stream is used to enhance the energy conversion process. In this case CO_2 takes part in the energy transition pathway which is portion of the utilization part in the CCUS procedure. In fact, the second part of this work concentrates on a case study where a high-efficiency fuel-cell based CHP is used to promote self-sufficiency within a medium-size plant located in Torino (IT). The 174 kWe Solid Oxide Fuel Cell (SOFC) produces energy from biogas with an electrical efficiency above 53% and zero pollutant emissions to the atmosphere. The system will cover around 30% of the WWTP electrical load. (Frontiers).

1.4 Power-to-fuel through carbon dioxide re-utilization and high-temperature electrolysis: technical and economical comparison between synthetic methanol and methane

E-fuels are synthetic fuels, resulting from the mixture of ‘green or e-hydrogen’ formed by the electrolysis of water with renewable electricity and CO_2 captured either from a concentrated source (e.g., flue gases from an industrial site) or from the air (via direct air capture, DAC). E-fuels are also described in the literature as electrofuels, power-to-X (PtX), power-to-liquids (PtL), power-to-gas (PtG) and synthetic fuels [38].

1.1.1. Feedstock-related technologies

Hydrogen electrolysis

E-hydrogen (also called ‘green hydrogen’) is used as a feedstock for producing e-fuels. It can also be a final product in itself. It is produced by electrolysis from water.

Different electrolysis technologies can be used for producing hydrogen. These include low-temperature (50 to 80°C) technologies such as an alkaline electrolysis cell (AEC), proton exchange membrane cell (PEMC), or high-temperature (700 to 1,000°C) processes using a solid-oxide electrolysis cell (SOEC) [39].

CO_2 capture

The production of e-fuels requires CO_2 which can be obtained from various sources including biomass combustion, industrial processes (e.g., flue gases from fossil oil combustion), biogenic CO_2, and CO_2 captured directly from the air. E-fuels production routes consist of e-hydrogen reacting with captured CO_2, followed by different conversion routes according to the final e-fuel (such as the methanization route for e-methane; methanol synthesis for e-methanol. E-fuel costs are currently relatively high (up to 7 euros/liter) but are expected to decrease over time due to economies of scale, learning effects and an anticipated reduction in the renewable electricity price; this is expected to lead to a cost of 1–3 euros/liter (without taxes) in 2050. therefore be 1–3 times higher than the cost of fossil fuels by 2050. The most important drivers for the future cost of e-fuels are the costs of power generation and the capacity utilization of conversion facilities [39].

E-fuels advantages:

The main advantages of these low-carbon fuels are [39]:

- E-fuels achieve a significant CO_2 reduction versus their equivalent fossil-based fuels, offering a compelling complementary alternative for low-CO_2 mobility
- E-fuels have a higher energy density compared to electricity and can thus be used in the aviation and shipping sectors where no electricity-based alternatives can be found in the short to medium term.
- Liquid e-fuels are easier (and relatively inexpensive) to store, and transport compared to electricity. They can be kept in large-scale stationary storage over extended periods, and mobile storage in vehicle tanks, which can compensate for seasonal supply fluctuations and contribute to enhancing energy security.
- Existing infrastructure can remain in use for transportation and storage (for example, gas transport networks, liquid fuels distribution infrastructure (pipelines), filling stations, storage facilities, and the entire rolling stock and fuel-based vehicle fleets).
- Some e-fuels could be deployed immediately across the whole transport fleet without any major changes in engine design. Liquid e-fuels are an alternative technology for reducing GHG emissions in both existing and new vehicles without requiring the renewal of the fleet.
- A high blending ratio is potentially possible when adding methane to natural gas, and liquid e-fuels to conventional fossil fuels, provided they meet the corresponding specifications.
- E-fuels would likely have positive impacts on environmental air quality because of the favorable combustion characteristics of the molecules produced.
- Finally, these synthetic molecules could be used also as precursors of other chemical processes and products, widening their market capabilities.

In the analysis of our work, two different plants are considered to produce synthetic fuels from hydrogen and CO_2. Both plants have been assessed from a technical and economic outlook.

Examining the methane production plant (Fig. 12), the great exothermicity of the reaction allows for an exceptional thermal integration between the fuel synthesis and the steam generation, minimizing and making almost zero the external heat requirement. The strong thermal integration, combined with the high conversion reached within the catalytic reactors, leads to high conversion efficiency (≈ 77%). On the other hand, for the methanol production (Fig. 13) a higher reaction pressure is required. Therefore, if the higher reaction pressure is combined with the minimal heat available from the reactor, the efficiency of the system is diminished (≈ 58%) because of the larger demand for external energy. The need of higher pressure for methanol production means that the initial investment and O&M costs are greater [40].

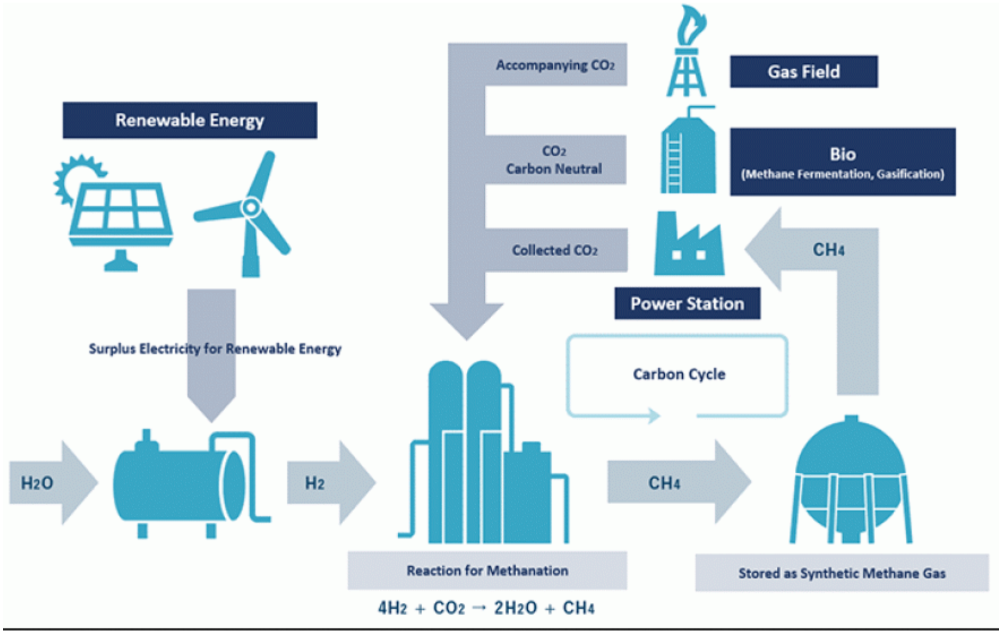


Fig. 12. Synthetic Methane from captured CO_2 using renewable energy [41]

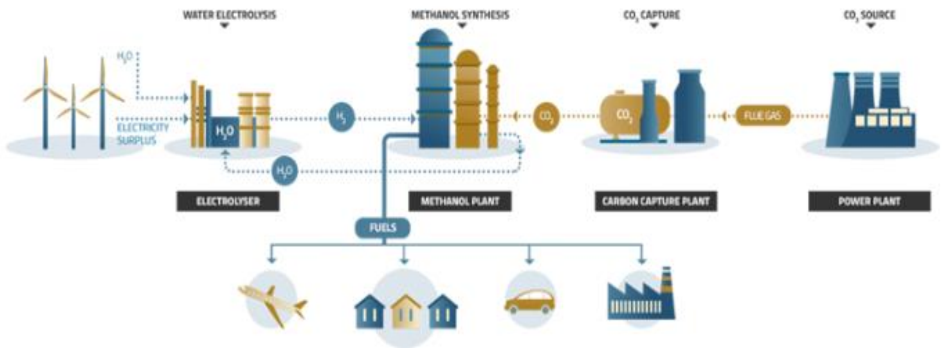


Fig. 13. Methanol fuel from CO_2- Synthesis captured CO_2 using surplus electricity [41]

When evaluating a sensitivity analysis, it was visible that the two studied systems present similar economic performance, unlike the difference between the efficiency of the two analyzed concepts, as the marked cost of the two-fossil counterpart (fossil methane and fossil-produced methanol) are different.

It was concluded that, to produce an economically attractive market for e-methane and e-methanol, in the present market conditions, the production plants should maintain a utilization factor of approximately 50%, the cost of SOECs should be near to 1050 €/kW and the electricity required to run the system needs to be supplied from renewable sources at a low cost (below 40-50 $/MWh) [40].

1.5 Mineral carbonation of high calcium fly ash

The work also examines the process of mineral carbonation (MC), a carbon capture utilization and storage (CCUS) technology that can capture large quantities of CO_2 and convert it into stable carbonate products that can easily be used in the concrete market. The focus of this investigation is the process of mineralizing fly ash (FA) by CO_2, two underutilized by-products formed at coal power plants, with the purposes of creating carbonated fly ash (CFA). CFA is a commodity that can permanently capture CO_2 but also has the advantage to be a complementary cementitious material used in the concrete/construction industry.

The evaluation of the work brings forward pragmatic evidence that MC production has the potential to deliver net positive revenue and its commercial feasibility is a realistic venture. However, the prospective of a new direction of cementation by the carbonation of FA is still maturing but with great potential for accelerated commercialization. The intensification of environmental and economic benefits generated by this new pathway for cementation are substantial if compared to the current methods of using FA in the construction industry. Yet, existing carbon policies, especially those referring to S&R, are shown to have a weak influence in the advancement of this enterprise. Well-designed policies can help start and build markets for CCUS technologies; moreover, they will play an important role in the future success of these innovations.

MC technology is one type of CCUS technologies that has the capacity of capturing and storing CO_2 while transforming it to solid inorganic carbonates (e.g., calcium and magnesium carbonate minerals) by means of chemical reactions. It is one of the few CCUS alternatives that results in permanent storage of CO_2 as a solid, with no need for long term monitoring [42]. Due to the product's stability over long periods of time it makes it ideal for the construction industry (Fig. 14); furthermore, it eliminates the concern of potential CO_2 leaks that could pose safety or environmental risks [43].

However, MC reaction progresses at an extremely slow rate under natural ambient conditions, to the degree that it limits the realization of any economic benefits of CO_2 sequestration [44]. The process could be enhanced and industrially applied to fix gaseous CO_2 into a solid carbonate regulating the operating variables and accelerating the kinetic of the process [45]. Currently there are different techniques to carry-out this endeavor; nevertheless, in all these cases, the process is referred as accelerated carbonation.

The use of fly ash has great prospective to diminishing GHG emissions by reducing mining activities, reducing CO_2 creation during the fabrication of materials that can be replaced by fly ash (e.g. Portland cement), curtailing the disposal problem usually in storage ponds and waterways, and aiding in the development of land utilization [46]. Moreover, with the necessity of controlling the emissions of CO_2 at local point-source, the use of coal combustion fly ash as a feedstock for CO_2 storage, has the benefit of on-site application at coal- fired power plants [47]. In this way the costs for carbon capture and storage, transfer, disposal, and treatment are reduced. Consequently, the final carbonated product is much safer for disposal or has the potential for re-use as a construction material or additive [48].

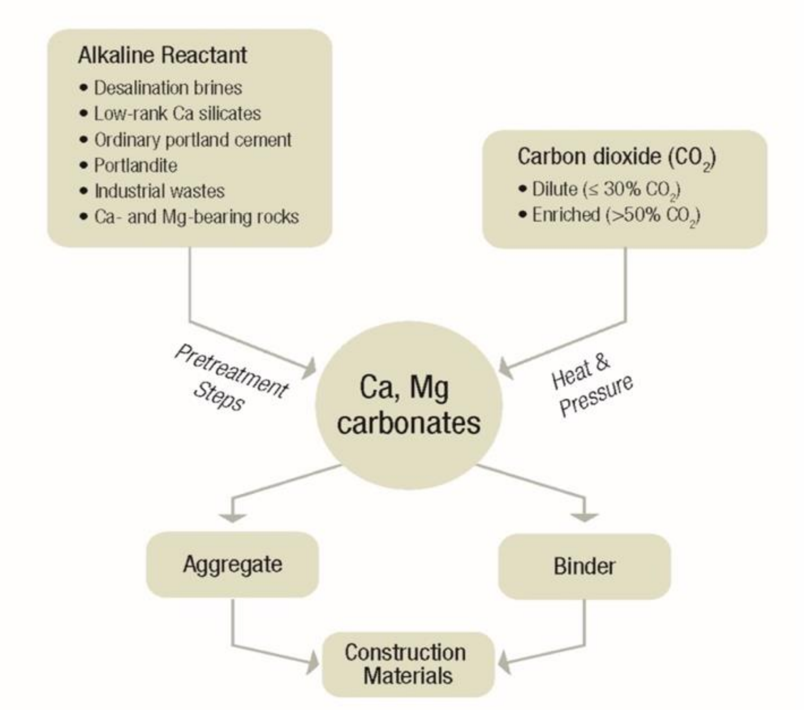


Fig. 14. Cost breakdown for e-fuels [5]

1.6 Carbonated Fly Ash Markets

The biggest near-term prospect for utilizing CO_2 is in cement used in concrete materials [49]. This is because of the large volume of these materials used commercially, their permanence, and the favorable chemistry that revolves around it. The billions of tons of CCUS potential in cement denote low-margin, highly standardized markets that are challenging to penetrate with new products [50]. Successful businesses to date have concentrated on making incremental modifications to traditional concrete formulation to abate the acceptance challenges, or on niche markets. Sizeable infiltration into the billion-ton global cement market will be very slow by this scheme. On the other hand, the use of carbonated solids, such as CFA, does not face such significant difficulties to enter the market, but does face significant cost burdens. With building materials being so economical, even in high-priced markets like California, it is unlikely that an industrial process making a CO_2 -based product will be competitive simply on price. For a type of business like this to flourish, long-term policy frameworks need to be established.

The billions of tons of prospective market and carbon mitigation also seem to require important technology development to be accessible. Direct CO_2 utilization as an additive in conventional products is the most technologically mature approach, and if regulatory acceptance can be realized, this method could utilize certain percent CO_2 by weight of concrete in construction applications where the "green" approach of the product is valued. With the EU, US, and China all showing signs of such valuation, this market will most likely expand. Especially in the EU, cement manufacturers are reporting their carbon footprints and contending to lower them. This effort is largely focused on more efficient clinker production and using less clinker, which has resulted in a 22% reduction in carbon footprint for the European manufacturer Heidelberg Cement since 1990 [51]. Efforts such as this will have a major impact on overall emissions, and as efficiency limits are reached, these companies may be expected to take on new carbonation tactics to continue their reductions.

1.7 Policies and Regulatory Framework

The case for policies to support CCUS technologies and carbon-based products is strong. There is a need to explore both incentives and credits as well as carbon price.

A carbon price can create enticements for CO_2 utilization in two ways. First, capturing CO_2 and using it in an economically valuable product could be the cheapest compliance strategy for some emitters. In the short- term this may be unlikely in most cases due to the high cost of CO_2 capture and conversion [52]. However as capture and utilization costs drop, there will be more occurrences in which this is a company's best compliance approach. Second, a carbon price may help incentivize private-sector investments in research and development on CO_2 utilization, if market participants expect the price to endure for the medium or long term [53].

Last year's climate conference in Katowice failed to agree on a rule book for market-based cooperation of how to make NDCs (nationally determined contribution) more uniform under the Paris Agreement. However, market-based mitigation policies are spreading around the world and carbon pricing initiatives at national and subnational level are being complemented by emerging international market schemes [54]

CO_2 utilization can be pursued to create products using new methods, materials, or feedstocks. In many cases, the products will need to follow existing codes and standards to be accepted in the marketplace. Often, there can be barriers within the codes and standards framework that dissuade products made using new technologies [55]. Codes and standards are typically overseen by members of government and industry and developed by consensus-based and voluntary commissions. Often, there are few incentives to update or expand existing standards. Further, even if the willingness exists, the changes to the regulatory framework can occur slowly. A process extending to 10 years is not unusual. The route to acceptance under codes and standards can be long enough to discourage the entrance of new technology into the market [56].

1.8 Thesis Plan

I. Chapter 1: Introduction and Overview

Describes the main goal of this work. It gives an overall view of each of the chapters contained in this document as it related to CO_2 global management, based on renewable energy technologies and processes (RETP), that have the likelihood to be commercialize within the next ten years. It shows three different archetypes of renewable energy technologies which are collected under the umbrella classification of CCUS. Furthermore, it discusses the markets, business opportunities, policies, and the status of renewable energy technologies during the Covid-19 pandemic.

II. Chapter 2: State of the art for CCUS technologies

Examines three emerging RETP (i.e., biogas & fuel cells, synthetic fuels, mineral carbonation of fly ashes) that fall into the CCUS paradigm and are either special, relatively new, or advanced forms of the mainstream energy sources. Each RETP sources' explanation is followed by its market share, challenges, implications for increased adoption, future prospects, and drawbacks.

III. Chapter 3: Biogas production and utilization at full-scale wastewater treatment plant

Discusses a particular case related to the use of a CO_2-blended gas in the processes of energy production using high temperature fuel cells such as SOFC. The use of CO_2 added to a carbon containing gas (i.e., natural gas or biogas) can have a positive effect on the process driven by the electrochemical machine, both in terms of preservation of the anodic electrode and in terms of global energy balance of the process.

IV. Chapter 4: Power-to-fuels through carbon dioxide re-utilization and high-temperature electrolysis: A technical and economical comparison between synthetic methanol and methane

This chapter presents some pathways to alternative mid- to long-term CCU options, specifically, the capture and transformation of CO_2, to produce sustainable, synthetic hydrocarbon or carbonaceous fuels (e.g., e-methane and e-methanol), mainly for the transportation industry.

V. Chapter 5: Mineral carbonation of high-calcium fly ashes, business opportunities, and policies & regulations related to this CCUS technology

This chapter reviews the process of mineral carbonation (MC), a CCUS technology that can capture large quantities of CO_2 and convert it into stable carbonate products that can easily be used in the concrete market. The focus of this investigation is the process of mineralizing fly ash (FA) by CO_2, two underutilized by-products formed at coal power plants, with the purposes of creating carbonated fly ash (CFA). CFA is a commodity that can permanently capture CO_2 but also has the advantage to be a complementary cementitious material used in the concrete/construction industry. Additionally, it discusses potential business opportunities and policies and regulations related to this rising renewable energy technology and process.

VI. Chapter 6: CCUS emerging technologies and processes market

It examines the potential commercialization of CCUS technologies by identifying four major markets and eight product categories critical to driving further investments and innovation at an accelerated pace. Funding and incentives are necessary for most of these products to accelerate development and achieve full-scale commercial roll out capability. The major markets and product discussed in this chapter are: (1) Markets- Building materials, chemical intermediates, fuels, polymers (2) Products- carbonate aggregates, methanol, formic acid, syngas, liquid fuels, methane, polyols and polycarbonates.

VII. Chapter 7: Conclusions

This chapter depicts the overall denouement of CCUS technologies, their market, policies & regulations, and the influence of the Covid-19 pandemic in the present and future status of RETP CCUS.

State of the Art for CCU Technologies

CCUS refers to a group of technologies that comprises the capture of CO_2 from large point sources including power generation or industrial facilities that use either fossil fuels or biomass for fuel; distributed sources (e.g., CO_2 concentrated in the air through the direct air capture technology), and biological sources (e.g., anaerobic digestion biogas undergoing an upgrading process often leaves a concentrated CO_2 stream as by-product), or from bio-syngas coming from the gasification of biomass of mixed origin [57] [58]. If not being used on-site (ex-situ), the captured CO_2 is compressed and transported by pipeline, ship, rail or truck to be used in a variety of applications or injected into deep geological formations (including depleted oil and gas reservoirs or saline formations) which trap the CO_2 for permanent storage. The extent to which CO_2 emissions are reduced in near terms depends on how much of the CO_2 is captured from the point source and whether and how the CO_2 is used (Fig. 15) [59].

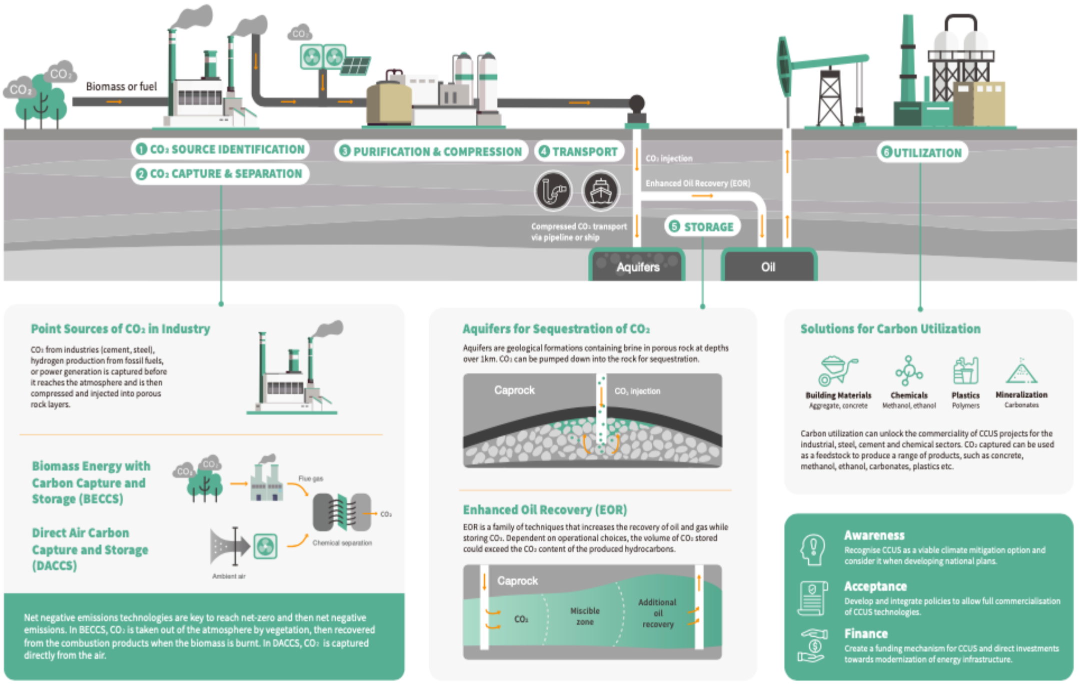
The term CO_2 utilization' refers to the use of CO_2, at concentrations above atmospheric levels, directly or as a feedstock in industrial or chemical processes, to produce valuable carbon-containing products [60].

Carbon utilization technologies convert gaseous carbon waste feedstocks (carbon dioxide or methane) into a wide range of commercial products and applications [61]. Generally, CCU can be categorized into three main pathways: mineral carbonation to produce construction materials, chemical conversion to produce chemicals and fuels, and biological conversion to produce chemicals and fuels. Methane utilization pathways include chemical and biological conversion to produce chemicals and fuels, as well as the direct use of methane as a fuel [62]. These technologies have the potential to transform waste streams into resources, reduce greenhouse gas emissions, and in some cases generate positive economic returns (Fig. 16) [63].

The process of CO_2 utilization is receiving increasing interest from the scientific community. This is in part due to climate change concerns and partly because utilizing CO_2 as a feedstock can result in a less expensive or cleaner production process compared with using conventional hydrocarbons [64]. CO_2 utilization is often fostered as a way to reduce the net costs—or increase the profits—of reducing emissions or removing carbon dioxide from the atmosphere, hence, a way to assist the scaling of mitigation or removal efforts [65].

The landscape of CCU is multifaceted and diverse. It involves an extensive array of applications (e.g., conversion to building materials, conversion to liquid fuels), technologies (e.g., electrochemical conversion using fuel cells, thermal catalysis), energy requirements (i.e. exothermic vs. highly endothermic), and settings (i.e. large industrial sites vs. distributed applications) [66].

It seems that there is enough potential and opportunity to grow commitment of resources into CCUS. It also appears that planning and investment decisions remain hindered by a lack of information, the dynamic nature of the technology, markets, and the changing policy landscape [67].



CO_2 from industries (cement, steel), hydrogen production from fossil fuels, or power generation is captured before it reaches the atmosphere and is then compressed and injected into porous rock layers.

Net negative emissions technologies are key to reach net-zero and then net negative emissions. In BECCS, CO_2 is taken out of the atmosphere by vegetation, then recovered from the combustion products when the biomass is burnt. In DACCS, CO_2 is captured directly from the air.

Aquifers are geological formations containing brine in porous rock at depths over 1km. CO_2 can be pumped down into the rock for sequestration.

EOR is a family of techniques that increases the recovery of oil and gas while storing CO_2. Dependent on operational choices, the volume of CO_2 stored could exceed the CO_2 content of the produced hydrocarbons.

Carbon utilization can unlock the commerciality of CCUS projects for the industrial, steel, cement and chemical sectors. CO_2 captured can be used as a feedstock to produce a range of products, such as concrete, methanol, ethanol, carbonates, plastics etc.

Recognise CCUS as a viable climate mitigation option and consider it when developing national plans.

Develop and integrate policies to allow full commercialisation of CCUS technologies.

Create a funding mechanism for CCUS and direct investments towards modernization of energy infrastructure.

Fig. 15. Carbon Capture, Utilization and Storage (CCUS) [61]

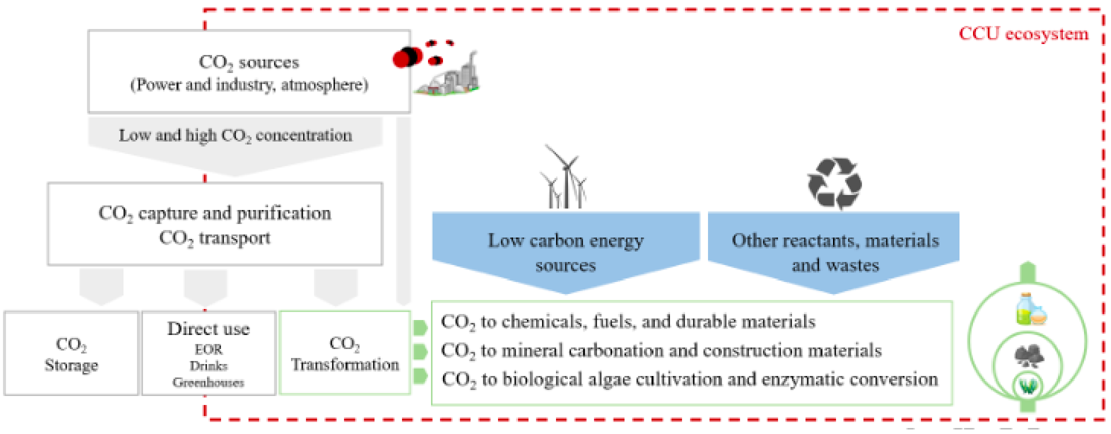


Fig. 16. CO_2 utilization ecosystem [68]

Carbon Capture Technologies

Meeting international climate goals, including net-zero emissions, will surely require some form of carbon removal. Carbon removal can neutralize or offset emissions where direct mitigation is currently technically challenging or excessively expensive, such as some industrial processes and long- distance transport [58]. Bioenergy carbon capture and storage (BECCS) and direct air capture storage (DACS) are an energy sector contribution to carbon removal and, if successfully deployed, can also mitigate slower progress in emissions reductions outside the energy sector [69]. Another key attraction of CO_2 capture technology is that it can be retrofitted to existing plants, many of which have been recently constructed or existing plants which permits have been renewed [70].

CO_2 is created during combustion and the type of combustion process directly affects the choice of an appropriate CO_2 removal process. There are three main CO_2 capture systems associated with different combustion processes, namely, post-combustion, pre-combustion and oxyfuel combustion (Fig. 17) [9].

- pre-combustion: based on the scaled industrial processes for the production of hydrogen and chemical commodities fuel feedstocks (i.e., coal and natural gas) are converted into syngas (H_2 and CO) via gasification, steam reforming, auto thermal reforming, or partial oxidation and then CO is transferred into CO_2 by water, with more hydrogen produced (the so-called water–gas shift reaction, WGS), followed by carbon capture system to remove CO_2. After CO_2 is captured, the hydrogen-rich fuel gas is utilized for power and heat generation such as boilers, gas turbines, and fuel cells [71].
- post-combustion: to capture CO_2 in the exhaust gases once the fuel has been fully burned with air. The commercially available post-combustion capture process is the chemical absorption-based aqueous amine solution, such as 30% monoethanolamide (MEA) solution. Post-combustion is considered as a more viable capture option for existing coal-fired plants [71].
- capture in oxy-combustion involves the combustion of fuel feedstocks in a nearly pure oxygen (95–99%) or O_2– CO_2–rich environment, resulting in a flue gas with very high CO_2 concentration, where the capture of CO_2 is thus normally not needed, and CO_2 is basically ready for sequestration. However, in order to obtain nearly pure oxygen (>95%) usually a cryogenic air separation unit is required for oxygen separation from air, which makes the whole process costly [71].

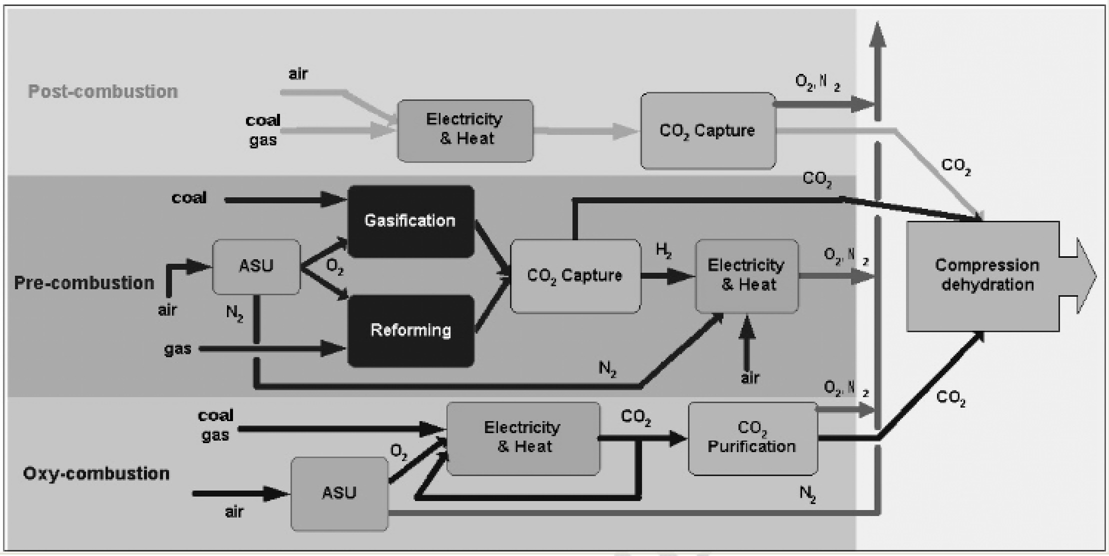


Fig. 17. CO_2 Capture Processes [9]

Extensively used cleanup technologies for methane or CO_2 can be generally split into four classes: (i) chemical absorption with basic media, normally aqueous, or physical absorption in liquid media; (ii) application of low temperatures (cryogenic); (iii) adsorption on a solid surface, followed by later removal under a temperature and/or pressure change; and (iv) membrane separation [9].

Within these categories are a numeral of specific processes, prominent by the solvent, sorbent, or membrane used; processing conditions; and subsequent purity of the desired products(s). Selection of a particular process is greatly dependent on the specific gas stream to be treated and the conditions required for the purified gas stream. Each cleanup system has distinctive features, advantages, and disadvantages which comprise energy consumption, capital costs, and the production of by-product streams of contaminated cleanup media for removal [72].

Carbon Dioxide Utilization (CO_2U)

CO_2U is the use of CO_2 to produce or generate economically valuable products or services [73]. A wide range of CO_2 utilization technologies are reviewed in this chapter, including CO_2 to chemicals, fuels, and durable materials, CO_2 to mineral carbonation and construction materials, as well as CO_2 to biological algae cultivation and enzymatic conversion (Fig 18).

Enhanced oil recovery (EOR), enhanced coal-bed methane (ECBM), and enhanced geothermal system (EGS) [74], are excluded from this work. Furthermore, CO_2 has also been used as refrigerant, as an extractive solvent, and as an additive in food and beverage products; as technologically mature processes that do not involve chemical transformations [75], these products are also outside the scope of this work.

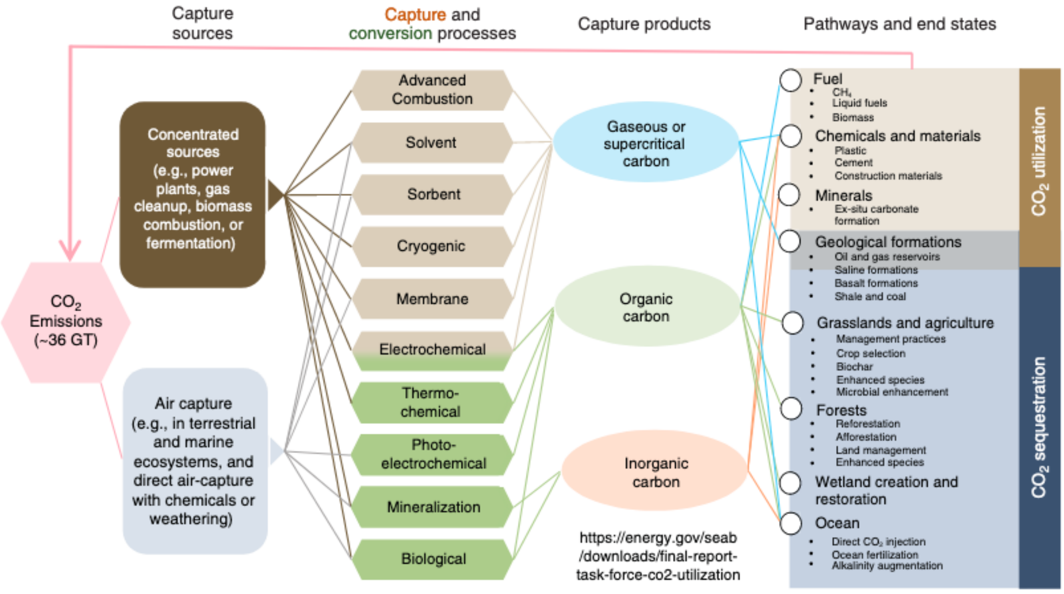


Fig. 18. Options for reducing CO_2 emissions or capturing emitted CO2 from the atmosphere [63]

The ranges of CO_2 utilization cover both direct and indirect applications. CO_2 can be naturally converted into materials via photosynthesis, ultimately producing biomass. Direct or technological use of CO_2 includes applications such as the extraction of compounds with supercritical CO_2, dry cleaning, and food industry uses, among others [76]. Indirect application use takes place given the fact that carbon free energy from renewable sources is available, captured CO_2 can be converted into useful commodity materials, chemicals, and fuels that are currently produced from fossil fuels, such as oil and natural gas, using engineered chemical and biological processes [68]. Within indirect applications, carbon dioxide is transformed through conversion processes into value-added products (thermo-/electro-chemical and biological conversion of CO_2). This results in secondary compounds that can substitute their conventional counterparts, such as building materials, cement, CO_2-cured concrete, fuels, and chemicals [77].

When carbon-based products are used to produce marketable commodities, CO_2U opportunities include both direct and indirect applications (Fig. 19). In the first case, the main direct uses of carbon dioxide include food and beverages production, metals fabrication, heat transfer medium in refrigeration and supercritical power systems, yield boosting for biological processes (e.g., algae harvesting and fertilizers production) and injection into reservoirs for either enhanced oil recovery (EOR) or enhanced gas recovery (EGR). In all the above-mentioned processes, the CO_2 molecule remains unchanged in its chemical form and is entrenched in the service production process after impurities are eliminated [78].

In the case of indirect applications, CO_2 is transformed through conversion processes that break its chemical bonds and permits its conversion (upgrade) into value-added products. Both thermocatalytic conversion, electro-chemical reduction and biological conversion of CO_2 can be applied. CO_2 is thus converted into [79]:

- secondary compounds that can substitute their conventional counterparts, such as building materials such as cement, concrete, and aggregates, or
- substitute fossil-based material with alternative synthetic resources, such as fuels and chemicals to be introduced in the chemical, transport and energy production sectors (e.g., methane, methanol, Fischer-Tropsch, olefins, ethanol) [80].

Often, the conversion to fuels and chemicals requires an intermediate step where syngas is produced (mixture of CO, CO_2, H_2 and CH_4), before conversion to the end-products [79].

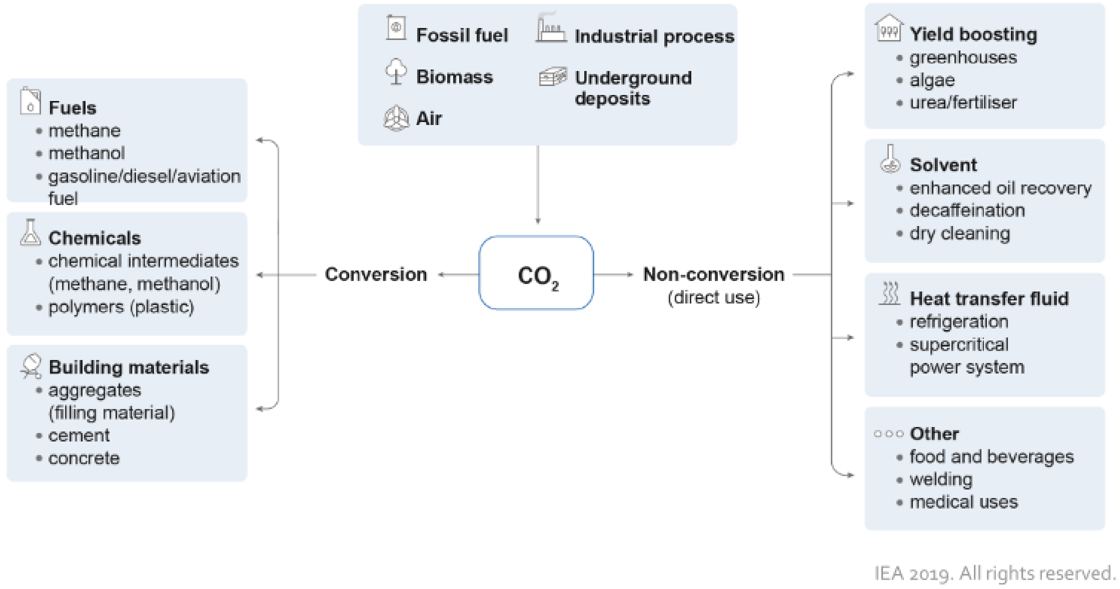


Fig. 19. Routes for direct and indirect conversion of CCU processes and sources of CO_2 [81]

Conversion Processes

2.3.1. Conversion to inorganic products (mineral carbonation)

Carbon dioxide into minerals and construction materials can follow in-situ and ex-situ processes [82]. In-situ CO_2 processes inject carbon dioxide into geological storages rich in silicates and alkaline aquifers. By reaction of CO_2 with minerals, calcium and magnesium silicates and carbonates can be obtained. With ex-situ applications, the carbonation process is chemically sustained in industrial plants, favoring the production of sodium, magnesium, calcium carbonates and sodium bicarbonate [83].

Mineral carbonation converts stable CO_2 into an even more stable form of carbon, typically a carbonate, which can be used to produce construction materials such as concrete [84]. Mineralization encompasses reaction of minerals (mostly calcium or magnesium silicates) with CO_2

to give inert carbonates [85]. The reaction to form carbonates itself requires no energy inputs, on the contrary, it releases heat, although significant energy is typically required to generate the requisite feed minerals [75]. The current blockage, however, for viable mineral carbonation processes on an industrial scale is the reaction rate of carbonation. Moreover, new formulations of materials such as concrete will require testing and property validation before being accepted by users and regulators for the market [86].

2.3.2. Chemical Utilization

It is possible to use CO_2 for the production of fuels and chemicals by reacting it with other molecules and/or providing electrochemical, photo-chemical, or thermal energy [87]. These conversions require catalysts to overcome kinetic barriers. Because carbon in CO_2 is in its most highly oxidized form, many of the resulting reactions are reductions, either through the addition of hydrogen or electrons [88]. Catalysts are important not only for making the transformation possible, but also for reducing the energy inputs to (ideally) the minimum amount dictated by the thermodynamics of the transformation, and discovery of appropriate catalysts and development of energy-efficient processes are current bottlenecks [75].

2.3.3. Biological Utilization

Biological conversion involves using photosynthetic and other metabolic processes inherent to plants, algae, bacteria, and fungi to produce higher-value chemicals [89]. Several factors have expanded the collection of bio-based products that can be synthesized directly from CO_2, including the large number of CO_2-utlizing microorganisms, genetic modification of microorganisms, and tailoring enzymatic/protein properties through protein engineering. Biological utilization has a large range of potential uses in the development of commercial products, including various biofuels, chemicals, and fertilizers. However, biological utilization rates and scalability remain challenges [88].

Conversion processes for specific carbon-base products

2.4.1. Conversion of CO_2 into fuels and chemicals

The challenges associated with the conversion of CO_2 into fuels and chemicals are primarily related to both its kinetic and thermodynamic stability [39]. CO_2 cannot be converted into commodity chemicals or fuels without significant inputs of energy and contains strong bonds that are not particularly reactive [90]. As a consequence, many of the available transformations of CO_2 require stoichiometric amounts of energy-intensive reagents. This can often generate significant amounts of waste and can result in large greenhouse gas footprints. The grand challenge for converting CO_2 waste streams into useful products is to develop processes that require minimal amounts of nonrenewable energy, are economically competitive, and provide substantial reductions in greenhouse gas emissions compared to existing technology [75].

2.4.2. Emerging technologies for CO2 conversion into commodity chemicals and fuels based on product

1. Methanol Production

Methanol (CH_3OH), usually is synthesized from syngas (H_2 + CO) obtained directly from fossil fuels [91]. A small amount of CO_2 (up to 30 percent) is generally added to the feed to improve performance [92]. This is successful in part because the mechanism of methanol production involves the initial conversion of CO and H_2O to CO_2 and H_2 via the water gas-shift reaction (Eq. 1). In fact, the development of methods to increase the amount of CO_2 in the syngas feed without causing a large decrease in methanol yield represents an opportunity to utilize waste CO_2 that is produced during syngas production. Although this strategy is only viable if excess H_2 is available, it could improve current technology and increase plant efficiency [88].

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad \text{(Eq. 1)}$$

The direct hydrogenation of CO_2 to methanol could provide a more sustainable synthetic route if coupled with low-carbon methods for the production of H_2 [91] [93]. Furthermore, the development of a practical method for the synthesis of methanol from CO_2 could also facilitate a transition toward a methanol economy, in which methanol is used either directly as a fuel or as a source of H_2 [94].

Researchers have developed several catalysts and reactors for direct hydrogenation of CO_2 to methanol, but high rates and high methanol selectivity have only been possible using high pressures (>300 bar) [91] [95]. The cost of this technology presently is not competitive with the cost of methanol synthesis from syngas [75].

Improved catalysts are critically needed if the direct hydrogenation of CO_2 to methanol is to replace methanol production from syngas. At this stage, significant amounts of research into the direct hydrogenation of CO_2 to methanol have focused on using heterogeneous copper-based catalysts that are closely related to those used for CO conversion to methanol [93]. In recent years there have also been a number of reports of catalysts for CO_2 hydrogenation to methanol which use metals other than copper and show promising activity [96] [97]. Two general challenges for catalyst development are product inhibition by water (the by-product of CO_2 hydrogenation) and poor selectivity because of the competing reverse water gas-shift reaction between CO_2 and H_2 to generate CO and H_2O. Once more efficient catalysts are developed, further attention can be given to factors such as stability, cost, sustainability, and scale-up potential. Additionally, although ultimately a large-scale catalyst for direct methanol hydrogenation will almost certainly be heterogeneous, research into homogeneous catalysts, which is occurring in the academic community, may prove valuable for guiding the development of heterogeneous systems and for niche applications where a small amount of methanol is generated, for example as fuel to power a portable device [95].

Finally, research is currently ongoing into the electrochemical reduction of CO_2 to methanol in which protons and electrons are used as the H_2 source. To date, however, most work reports the formation of methanol as a by-product [98]. Further exploratory and mechanistic research will be required to identify even more selective (and stable) catalysts that do not require organic electrolytes before electrocatalytic methanol production from CO_2 can be considered for larger-scale application.

Methane Production

Methane is widely used as a fuel and to make syngas [99]. Similarly, to methanol production, the synthesis of methane can be done exploiting the reaction between anthropogenic CO_2 and renewable hydrogen. Under equation (Eq. 2), the hydrogenation of CO_2 produces methane and water as by-product (Sabatier reaction) [100]. The operating temperatures are generally slightly higher than for methanol production and similar pressure values (250-400°C). The catalysts in this case are generally Ni-, Rh- or Ru-based [79] [101].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \text{(Eq. 2)}$$

Research continues on the design of improved catalysts [100]. At this stage, the hydrogenation of CO_2 to methane is not practical on a large scale and is unlikely to be so in the near future given the low price and abundant availability of methane from natural gas [88]. Additionally, there will be a significantly greater economic value in converting CO_2 to many other chemicals compared with methane. As for the aforementioned thermochemical CO_2-to-methane processes, at this time the electrocatalytic conversion of CO_2 to methane, despite continued progress in the development of more selective catalysts, probably will not be pursued on a large scale given the global availability of low-cost methane derived from natural gas [75].

Fuel (Hydrocarbon) Production

Given that the majority of CO_2 that is released in the atmosphere is from the combustion of fossil fuels, the development of methods to synthesize fuels from CO_2 could result in a closed carbon cycle, where increases in concentration of CO_2 in the atmosphere will be minimal [88]. This can only be achieved if the electricity or H_2 that is used to reduce CO_2 is generated from carbon-free sources, and if the carbon waste gases created by the combustion of the fuel are recaptured and reutilized [75]. In principle, methane and methanol could be used as fuels and systems for the conversion of CO_2 into these molecules are actively being pursued. Therefore, in this section only the state of technology for the conversion of CO_2 into hydrocarbon fuels with more than two carbons will be described. The Fischer-Tropsch process is used to convert CO and H_2 into liquid fuels and has been commercialized on a large scale [102]. One approach for producing fuels from CO_2 could involve initially electrochemically synthesizing CO from CO_2 and then in a second thermal step combining the CO with sustainably produced H_2 to produce fuels via the conventional Fischer-Tropsch process [75]. Alternatively, a significant amount of research is currently being performed to develop systems that can perform Fischer-Tropsch chemistry starting from CO_2 in a single reactor using a single catalyst. In this chemistry the first step is generally the reverse water gas-shift reaction to generate CO from CO_2 (Eq 1). This CO then reacts with H_2 to form liquid fuels through a mechanism based on the conventional Fischer-Tropsch reaction (Fig. 6) (Eq 20).

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_n H_{2n+2} + n\ H_2O \qquad \text{(Eq. 3)}$$

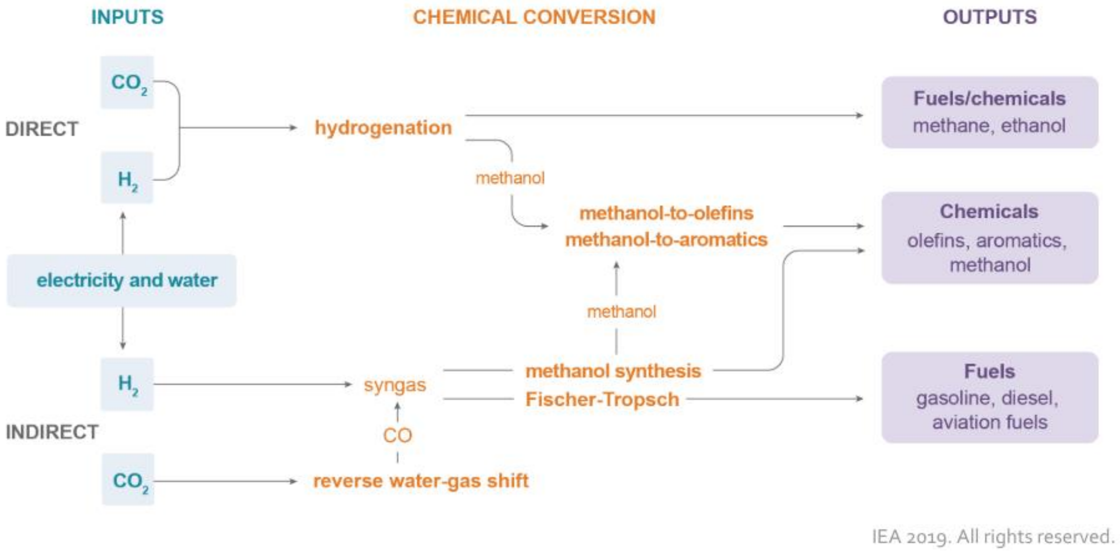


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Fig. 20. Ex. of routes for direct and indirect conversion of CO_2 into fuels and chemicals [81]

Construction Materials and Minerals

The conversion of CO_2, a low-energy molecule, into solid mineral carbonates is one of only a few thermodynamically favorable reactions involving CO_2 and can be accomplished at near-ambient temperatures. For this reason and because of the tremendous size of the construction materials market, mineral carbonation is considered to be among the largest and most energy-efficient routes for CO_2 utilization [75].

Fixation of carbon dioxide into minerals and construction materials can follow in-situ and ex-situ processes (Fig. 21) [103]. In-situ CO_2 fixation processes inject carbon dioxide into geological storages rich in silicates and alkaline aquifers. By reaction of CO_2 with minerals, calcium and magnesium silicates (Eq.4) and (Eq. 5) and carbonates can be obtained. With ex-situ applications, the carbonation process is chemically sustained in industrial plants, favoring the production of sodium, magnesium, calcium carbonates and sodium bicarbonate [79]. Such materials can be further utilized in cement production and construction processes (e.g., utilization of CaO, CO_2-cured concrete, building aggregates) [104]. Generally, the processes of carbonation of CO_2 generates heat, and so the formation of carbonates is favored at low temperatures [105].

$$\mathrm{CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2}\ \left(+90\,\frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}}\ \text{wollostonite formation}\right) \qquad \text{(Eq. 4)}$$

$$\mathrm{Mg_2SiO_4 + 2CO_2 \leftrightarrow 2MgCO_3 + SiO_2}\ \left(+89\,\frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}}\ \text{olivine formation}\right) \qquad \text{(Eq. 5)}$$

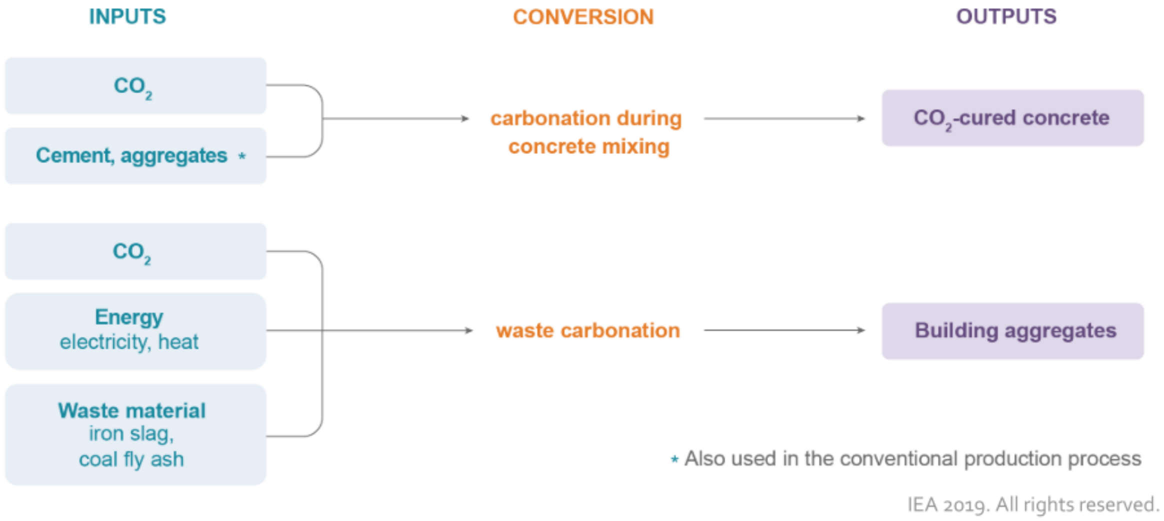


Fig. 21. Routes for the conversion of carbon dioxide into construction materials [81]

Biogas Production and Utilization at Full-Scale Wastewater Treatment Plant

The growing scarcity and increase demand for water, food, and energy are imminent threats the world is collectively facing. In order to tackle these problems, waste (e.g. wastewater and municipal waste, among others) is now being considered more as a resource than as a discarded source [106].

Intensive research efforts have been made to develop processes for converting methane into more valuable products. CO_2 reforming of methane shows noteworthy environmental and economic benefits by consuming two major greenhouse gases, carbon dioxide (CO_2) and methane (CH_4), to produce synthetic gas (i.e. syngas) ($CO+3H_2$), a key industrial intermediate [107].

Most synthesis gas is produced by the steam reform reaction (Eq. 1) in large furnaces to supply the necessary energy for this highly endothermic reaction (consumes heat $\Delta H = 206 \frac{kJ}{mol}$) [108].

$$\mathrm{CH_4} + \mathrm{H_2O}\ (\text{catalyst}) \rightarrow \mathrm{CO} + 3\mathrm{H_2} \qquad \text{(Eq. 1)}$$

Industrially, steam reforming is performed over a Ni/Al_2O_3 catalyst [109]. The typical problem is the tendency of carbon deposition on the catalyst. Consequently, steam reactors must be operated with higher H_2O/CH_4 ratios than the stoichiometric value. To reduce the carbon deposition, not only is an excess of water needed but also a high temperature of approximately 1073 ^{o}K must be utilized [58]. For this reason, steam reforming requires a large amount of fuel and very high heat fluxes.

Carbon dioxide can be considered an oxidizing agent for the oxidation of methane, in lieu of oxygen or water for the production of syngas via a reaction called CO_2/dry reforming of methane, (DRM) [110] (Eq.2).

$$\mathrm{CO_2} + \mathrm{CH_4} \leftrightarrow 2\mathrm{CO} + 2\mathrm{H_2}\ (\Delta \mathrm{H} = 247 \frac{\mathrm{kJ}}{\mathrm{mol}}) \qquad \text{(Eq. 2)}$$

DRM is one of the most important processes used in the production of syngas. In that case, DRM contains the most reduced form CH_4 combined with its most oxidized form of carbon CO_2. The DRM reaction is favored by low pressure, however, the strong C-H bonds (439 kJ mol-1) in methane leads to an endothermic process that requires high temperatures for CH_4 conversion [111]. However, this process is not widely used in the gas processing industries because of rapid catalyst deactivation due to carbon deposition [112]. DRM reaction needs high temperature in the presence of a metal catalyst, as reactions are extremely endothermic. The DRM process offers some advantages over SRM of methane, out of which the most significant is the production of syngas with low H_2/CO ratio, more suitable for synthesis of liquid chemicals and fuels. An archetypal application is the production of methanol and Fischer-Tropsch synthesis H_2/CO, which can be produced by DRM [113] [99]. DRM also significantly reduces the environmental aspect of the reaction, as methane and carbon dioxide are greenhouse gases (GHGs).

A particular case is related to the use of a CO_2-blended gas in the processes of energy production using high temperature fuel cells (like Molten Carbonate Fuel Cells – MCFC and Solid Oxide Fuel Cells – SOFC). In this case the use of CO_2 added to a carbon containing gas (e.g.., natural gas or biogas) can have a positive effect on the process driven by the electrochemical machine, both in terms of preservation of the anodic electrode and in terms of global energy balance of the process.

Carbon dioxide can be utilized to activate the reaction of DRM inside the stack of fuel cells, thus promoting three important effects:

- Protecting the anode from phenomena of carbon deposits.
- Transforming the methane molecule into "superior" molecules (H_2 and CO) for electrochemical reactions. These molecules are more active electrochemically than methane. The production of syngas can act as a suitable fuel in electrochemical machines such as high temperature fuel cells. Moreover, the DRM driven directly on the anode of a high temperature fuel cell will drive a reaction which is endothermic, hence, generating an effect of heat sink that reduces the need for external cooling and increases the overall efficiency of a system (e.g., SOFC system). In this context, considering the global thermal balance of these reactions; consideration needs to be given to the reverse water-gas shift reaction (RWGS) (Eq.3), which is mildly exothermic (produces heat, ($\Delta\mathrm{H} = -41\frac{\mathrm{kJ}}{\mathrm{mol}}$) , the Boudouard reaction (Eq.4), and the methane decomposition reaction (Eq.5) are side reaction in reforming [110] [114]:

$$\mathrm{H_2 + CO_2 \leftrightarrow CO + H_2O} \quad (\Delta\mathrm{H}^0_{298\mathrm{K}} = -39.5\frac{\mathrm{kJ}}{\mathrm{mol}}) \qquad \text{(Eq.3)}$$

$$\mathrm{2CO \leftrightarrow C + CO_2} \quad (\Delta\mathrm{H}^0_{298\mathrm{K}} = -171\frac{\mathrm{kJ}}{\mathrm{mol}}) \qquad \text{(Eq.4)}$$

$$\mathrm{CH_4 \leftrightarrow C + 2H_2} \quad (\Delta\mathrm{H}^0_{298\mathrm{K}} = 75\frac{\mathrm{kJ}}{\mathrm{mol}}) \qquad \text{(Eq.5)}$$

Kinetics

Although many researchers have led investigations on the reforming mechanism, there still are some contentions regarding the details of the precise reaction mechanism and the rate-determining steps (RDS) [115]. For example, the number of RDSs is still disputed by some scientists. Some researchers stated that the mechanism of the dry reforming reaction was one single RDS, while others testified a mechanism with two RDSs for the same reaction [116]. The main motives for the differences in the reported reforming mechanism can be credited to two facts: (1) the different supports and sponsors employed in the reforming reaction may result in the disparity of the reforming mechanism, which has been observed by some research groups; and (2) the mechanism investigation was conducted at different temperatures, which may remarkably affect the reforming mechanism and the RDS [117]. Several different kinetic models have been reported. Most of the kinetic models are based on the reversible dissociative adsorption on the catalyst active site to produce H_2, or on the reversible and dissociative adsorption of CO_2 on the support to yield CO [118].

Catalysts

Based on the above argument, it seems that the maximum activity and H_2/CO ratio and the minimum carbon deposition can be attained at high temperatures (e.g., higher than 817 °C). On the other hand, when the reaction occurs at high temperatures, high energy utilization makes this process impracticable for industrial applications [119]. The use of catalytic systems may lead to greater activity at lower temperatures and, consequently, the decrease of the energy consumption in the process, which would permit this technology to get closer to an economical process [120]. Thermodynamic calculations showed that the temperature needed for 50% CO_2 conversion in DRM without catalyst is 1035°C (1308 °K), but on the source of existing literature data, very high CH_4 and CO_2 conversions can be achieved in temperatures as low as 700 °C using catalytic systems [113].

Over-all, it has been acknowledged that the catalytic CO_2 reforming of methane has a bi-functional mechanism. CH_4 can be adsorbed and activated by the active sites of most of the transition metals, mainly groups VIII b of the periodic table, while CO_2 is adsorbed and activated by oxides [118]. Thus, the DRM reaction can be catalyzed by most of the transition metals supported on oxides [112].

Over the past two decades, concentrated efforts have been dedicated by many research groups to advance catalysts that can achieve high catalytic activity and stability with maximum H_2/CO molar ratio and minimum coke formation for DRM at low temperatures [112].

Notwithstanding numerous publications and evaluation between different catalysts in diverse reaction conditions in the literature, there still are some contentions regarding the main active and stable catalyst in DRM [99]. Although, the performances of catalysts can be affected by an array of factors other than composition, such as content of active components, preparation methods, calcinations ambient, calcinations temperature, reduction and activation measures, precursors of active components, etc., it is well acknowledged that nickel has the best catalytic performance among all examined catalysts except for the noble metals [112]. In the case of noble metal catalysts, some researchers stated that Pd showed the highest activity and stability while others reported that Rh and Ru catalysts revealed the highest activity and stability among the noble metals [121]. Likewise, there is an continuing disagreement between researchers concerning Ni and noble metals to choose which one has the best catalytic behavior during DRM [120]. Many researchers described higher catalytic activity for Ni-based catalysts in contrast with metals catalysts, while some other researchers reported that noble metals have enhanced catalytic activity than Ni-based catalysts [122]. Undeniably, on a mole for mole basis, Ni is about 10,000 times cheaper than Pt and 200 times cheaper than Pd [123]. Therefore, from sensible and industrial viewpoints, Ni-based catalysts are the most attractive and promising for DRM [122].

Ni-based catalysts have a propensity to experience deactivation via carbon deposition and sintering and hence significant efforts have been devoted to improving these catalysts [120]. Tactics to advance the activity and stability of Ni-based catalysts for DRM have concentrated mostly on the breakthrough of improved supports and suitable promoters/Ni-based catalysts [122]. Researchers conveyed both positive and negative results for the addition of a second and/or third metal (bimetallic and tri-metallic) on the implementation of catalysts. SiO_2 and Al_2O_3 are two of the most examined catalyst supports with high melting points and specific surface areas. MgO, CaO, CeO_2, La_2O_3, TiO_2 and ZrO_2 are also frequently studied [119].

The effects of the precursor, preparation circumstances, type of reactor (including plasma reactors, fixed and fluidized bed reactors, membrane reactors), heating method, reduction method, feed composition, and space velocity on the reforming reaction were examined [110]. Nonetheless, there have been accounts showing that the application of plasma may be a suitable method to induce high conversions of CO_2 and CH_4. However, plasma technologies are very expensive, and the utilization of electrical current to produce plasma may be counterproductive to the carbon balance [110].

Production of biogas

The activity related to the use of CO_2 inside an energy production process has been developed in the case of a stream of biological origin (so, Carbon neutral) and containing a large amount of CO_2: biogas produced in wastewater treatment plants (WWTPs) with the goal of converting these plants as net energy producers. The concept revolves around researching technological measures to upsurge self-sufficiency in WWTPs. This feat is deemed to be an achievable target since wastewater already contains two to four times the amount of energy needed for the wastewater treatment process.

The organic matter contained in the wastewater can serve as a source of energy to eventually manage the WWTP. Organic matter is retrieved as sludge, which is processed in large tanks called anaerobic digesters (AD) to produce biogas. The in-situ accessibility of biogas provides the opportunity to cover a substantial portion of WWTPs electricity and thermal demands. Biogas can be transformed into electrical and thermal energy by utilizing high temperature fuel cell generators.

Different studies have focused on solutions to increase the energy efficiency of WWTPs. Reducing energy consumption and increasing the efficiency of energy production are both required to have positive energy WWTPs. Measures to reach self-sufficient WWTPs are listed below:

Process optimization: this approach consists in installing smart meters [7] within the plant and developing control systems for the optimal operation of aeration systems and water pumps (aeration is part of the secondary biological treatment, which takes more than 50% of the overall electrical consumption [124] [125]. EPRI has estimated that, in wastewater facilities, 10-20% energy savings are possible through better process control and optimization [56].

Enhanced biogas yield: currently, anaerobic digestion (AD) biogas can only provide around 50% of the total energy consumption. However, sludge pre-treatments can lead to an increase of the biomethane yield [126].

Efficient on-site combined power and heat (CHP) generation: the use of fuel cell systems (e.g., SOFC plants) can increase further the on-site electricity generation, which is key to self-sufficiency.Co-digestion of sludge with food waste is also an interesting option to increase the overall biogas output.

In the next section (3.4) a case study called DEMOSOFC will be presented; a medium-scale (174 kWe) distributed Combined Heat and Power (CHP) system based on Solid Oxide Fuel Cell (SOFC) and fed with locally available biogas produced in an industrial-scale wastewater treatment plant.

3.3.1. Technical assessment of a cohesive anaerobic digester and solid oxide fuel cell (SOFC) system

Globally there is an increasing focus on looking for alternative technologies able to generate power, at the same time respecting the environment and saving energy.

It is in this context that electrochemical fuel cell devices meet with great approval, owing to their high energy efficiency with reduced environmental impact generators. When these are fed by a derived biological gas the energy system becomes relevant in the context of environmentally sustainable energy production. Biogas is the product of biological processing of waste with no economic value and compared to other fuels has the great advantage of being renewable and free from NMHC (non-Methane Hydrocarbons). It is recognized by the United Nations Development Program as one of the most important decentralized energy resources [127].

The technique of anaerobic digestion is widely used for biogas production, whereby the degradation of organic substances take place in an oxygen-free environment.

The selection and evaluation of the fuel cell is conducted in relation to the characteristics of the input fuel and to the energy performances, power, and efficiency, achievable from its feeding.

Biogas production plants from different sources are becoming more and more diffused around Europe. The biogas produced can be split in two streams and sent:

- To an upgrading system (to be converted in high CH_4 containing gas)
- To high-efficient conversion device (SOFC) for electricity and heat production.

However, in both processes there is the need to manage the residual gases (exhaust from the SOFC and off gas from the upgrading system) in order to reduce CO_2 emissions in atmosphere. There is the possibility to combine the two residual flows for CCU, in order to transform a waste flow into a resource.

The potential of this type of system is the capability to produce not only heat & power (with very high efficiency), but also, green fuels and chemicals through a dedicated management of the CO_2 recovered from the system, all this starting from a renewable energy source like biogas.

As the DEMOSOFC case study will show, an anaerobic digestion plant is combined with a high temperature fuel cell system. This system was studied both from an energetic and environmental point of view, for the distributed generation of both electrical and thermal energy.

Case Study (DEMOSOFC)

The European project DEMOSOFC coordinated by Politecnico di Torino focuses on the installation of the first industrial size plant in Europe able to convert the sludge from a wastewater treatment process into clean and high efficiency energy by using SOFC technology that can use directly natural gas or biogas. SOFCs are the most efficient and fuel flexible devices among the different fuel cell types available. The total project budget is around 5.9 million euro and is financed by European Union with 4.2 million euro in the framework of the Horizon 2020 program.

The DEMOSOFC plant covers around 30% of the site needs (provided by the grid) and 100% of the thermal requirement. The system consists of the installation of three fuel cell modules able to co-produce 175 kW of electrical power and 90 kW of thermal power, with an electrical efficiency of 53%.

The system is installed in the SMAT Collegno wastewater treatment plant (Turin), where currently biogas is produced from anaerobic digestion of sewage sludge. Biogas – a renewable fuel – is first cleaned (Sulphur contaminants are removed) and then sent to the fuel cell where high efficiency electrical energy is produced (with an electrical efficiency up to 50%, while traditional competitors like engines and turbines reach only 35-38 %). The system is also cogenerative since the heat recovery from the exhaust gases is also performed (Fig.22).

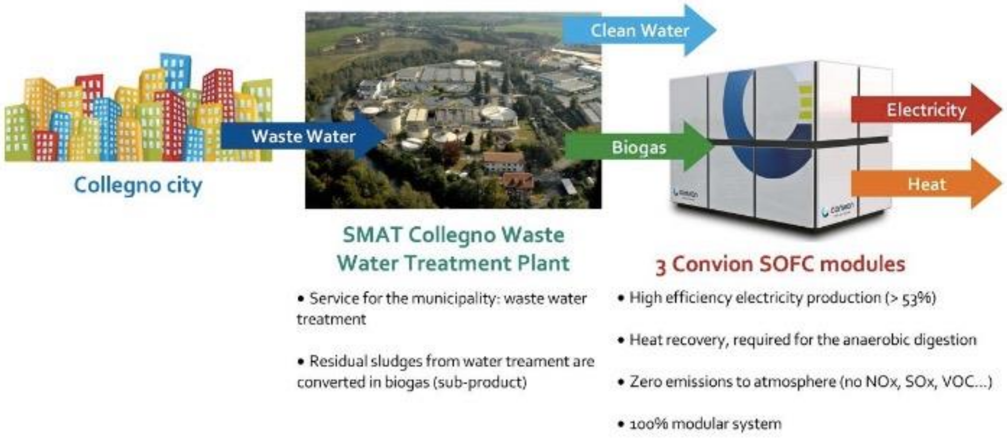


Fig. 22. Waste-to-Energy production system at SMAT's WWTP (DEMOSOFC)

From an energy point of view the system can demonstrate how Smart Fuel Cell (SFC) systems are a key driver for future energy plants, based on renewable fuels, with very high electrical efficiencies and total recovery of the processed elements (carbon, hydrogen and oxygen), trying to generate a new concept of dual-generation systems (i.e., heat and power).

Furthermore, while traditional cogeneration systems generate exhaust gases with CO_2 mixed with a high nitrogen flow, with related complications in the sequestration processes, in a SOFC systems exhausts from the anode side are free from nitrogen, leading an easy CO_2-capture through a simple condenser to remove water.

DEMOSOFC aims to carry the innovative concept at an industrial scale through a product/process ready for the commercialization. Currently, the process components are produced mainly in Germany, England, Italy, USA and Japan. The market interest on this new technology is thus clear and, thanks to synergies created by the European Agency FCH-JU, cooperation between industry and academy is strengthened. From the end user point of view, this specific application found its niche function within various forms of biogas plants [128].

Similar designed plants are currently operating in California, U.S.; however, these plants are fed by natural gas (methane). The innovative biogas feeding aspect of the project makes DEMOSOFC a strategic venture for Europe. Furthermore, its results can be replicated while helping the development and consolidation of the industrial and scientific area.

Analysis of waste treatment sector as a driver for SOFC cost reduction

Energy production is one of the biggest challenges Europe and the U.S. are currently facing It is mainly concerning to the subjects of policy and regulations that obstruct the development of renewables to the shortage of capital to fund the progress of new technologies [129]

A paradigm shift is currently changing our understanding of the need of technological innovations, supply, policies, and environmental deployment regulations for the successful growth of green technologies [129].

According to the European Commission, the delay of climate action would require additional investment expenditure of around € 100 billion /year between 2030 and 2050. Unfortunately this would not reduce investment needs before 2030 by a comparable amount [130].

The quick deployment of large-scale (> 10 MWs) [131] projects involving a new renewable energy technology with a low-carbon footprint is one of the European Commission's goals to achieve a low-carbon society in the near future [132].

In the U.S. as mentioned in the Annual Energy Outlook 2021 (AEO2021) [133], the U.S. Energy Information Administration (EIA) projected that the share of renewables in the U.S. electricity generation mix would increase from 21% in 2020 to 42% in 2050. Wind and solar generation are responsible for most of that growth. The renewable share is projected to increase as nuclear and coal-fired generation decrease and the natural gas-fired generation share remains relatively constant [133]. By 2030, renewables will collectively surpass natural gas to be the predominant source of generation in the United States. Solar electric generation (which includes photovoltaic (PV) and thermal technologies and both small-scale and utility-scale installations) will surpass wind energy by 2040 as the largest source of renewable generation in the United States [134].

3.5.1. General fuel cell background

A fuel cell (FC) consists of an anode and a cathode with an electrolyte in the middle that utilizes electrochemical reactions, rather than combustion, to produce energy (very similar to a battery). Consequently, GHG are significantly reduced; byproducts are only water, heat, and, a reduced amount of carbon dioxide - all of which can be re-used for other applications [135].

FCs are among the most promising clean energy technologies currently in existence [136]. They are expected to play a significant role in order to attain the EU's objective of achieving an overall 80% reduction in the EU emissions by 2050 (compared to 1990) [137]. In the U.S. the Fuel Cell & Hydrogen Energy Association (FCHEA) reported that FCs could reduce the nation's carbon emissions by 16% by 2050 and greater FC's deployment could also reduce carbon emissions in the U.S. transportation sector by 30% and lower NOx emissions by 36% [138]. Moreover, FC's have been drawing interest from the scientific community due to their high-energy efficiency; clean energy production, high power density, site and fuel flexibility, and uninterruptible power supply system, amongst other attributes [139].

There are different types of FCs, and they vary depending on their design, size, type of fuel they use to operate, and choice of electrolyte. SOFC, is one types of FC, and it can reach efficiencies of up to 60% when fueled with natural gas or biogas. WWTP facilities are, by nature, usually located close to populated areas, consequently making them large producers of biogas from sludge, which are a by-product of the water treatment activity [140]. Biogas is a mixture of methane and carbon dioxide (typically 60% CH_4 and 40% CO_2) and it is considered a clean fuel source to produce electricity and heat. WWTPs employ the process of anaerobic digestion (AD) to produce biogas. Anaerobic digesters are usually part of the WWTP system; therefore making these facilities very attractive to implement distributed generation (DG) applications [30]

3.5.2. The WWTP as a 'starting market' for the SOFC technology

WWTPs are producing biogas as a sub-product of the entire plant. Anaerobic digestion for biogas production is a way to stabilize the sludge flow and reducing its organic load: for this reason, biogas can be considered as a free fuel for the plant.

WWTPs are intensive energy consumers, especially concerning electricity needed to fuel the pumps and aeration systems. Consequently, the possibility of self-producing high efficiency energy and reducing grid-dependence is seen as a key driver for WWTPs to adopt circular technologies [141]. As mentioned above, SOFC systems show no emissions to atmosphere since no combustion of fuel is performed. This is another driver, especially in a future perspective, because of continuously reduced national and regional emission limits, especially for what concerning NOx, SOx, PM and organic compounds.

In short, WWTPs offer an attractive context to implement SOFCs as these plants offer the required biogas to fuel SOFC, while operating WWTPs requires vast amounts of energy. The SOFC technology thus allows translating a by-product in a productive energy source, thereby partially closing the loop of production, while simultaneously reducing the emission of harmful substances [142].

However, the main criticality related to biogas use in SOFCs is the need for a biogas cleaning system, which is a non-standard component required when biogas is fed to SOFCs. Compared to traditional CHP system, SOFCs are more sensitive to biogas contaminants such as Sulphur and siloxanes. Fortunately, biogas resulting from WWTPs shows relative low levels of contaminants further contributing to the attractiveness of WWTPs as a market opportunity to implement SOFCs. Because of a relative 'clean' biogas, SOFCs installations in WWTPs usually required only a single stage contaminants removal, by using adsorption materials [143].

Italy

Wastewater treatment plants often require significant amount of heat and power in order to operate, thus accounting for a large percentage of a municipal's energy cost [144]–[146]. In Europe, WWTPs account for more than 1% of the electrical consumption, with a total estimated electricity consumption of 15,021 GWh/year spread among 22,558 plants [32]. Furthermore, energy for wastewater treatment (WWT) is likely see a global increase of 20%-30% within the next 15 years due to increasing population and capita consumption, stricter discharge requirements, and aging infrastructure [147].

In the U.S. municipal wastewater treatment plants are estimated to consume more than 30 terawatt hours per year of electricity, which equates to about $2 billion in annual electric costs. Electricity alone can constitute 25-40% of a WWTP's annual operating budget and make up a significant portion of a given municipality's total energy bill [148]

The allure of introducing SOFC into the WWTP market goes beyond the advantage of fuel flexibility; for example [149]:

1. With WWTPs there is no need to build an entire infrastructure just to be able to incorporate a SOFC system. Therefore, the initial investment associated with the construction of incorporating the system is minimal in the whole scheme of things.
2. WWTPs already have a pool of experience professionals, which can operate and maintain the SOFC system [147].
3. The need for incorporating external sources of power to be able to operate is minimize when utilizing SOFCs. Because of the decreased use of imported electricity from the central electric power source, the load placed on the electric grid is minimized.
4. While traditional cogeneration systems produce exhaust gases with CO_2 mixed with a high nitrogen flow, with related difficulties in the sequestration processes, in a SOFC systems exhausts from the anode side are free from nitrogen, leading an easy CO_2-capture through a simple condenser to remove water [150].

As seen in Fig. 23, WWTP distribution in Italy is composed of a high number of micro and small plants, working with a reduced entering load, and few large size plants which are serving the capital cities or aggregation of medium size cities (Turin, Rome, Milan, aggregated Tuscany and Veneto cities). Total number of WWTPs in Italy is 5,672, and average entering load is 12,324 P.E. served. Production of biogas is currently performed in large system where traditional CHP systems show better performance. Internal combustion engines (ICEs) can show up to 42-43% efficiency when MWs size systems are installed. However, when smaller system are analyzed, the efficiency drops at around 35% making the initial investment less rewarding [151]. SOFCs in contrast are modular systems, which can guarantee a constant and high efficiency (higher than 50-55 %) at every size, from kW to MW size. These higher efficiency rates, combined with more flexible employability, makes SOFC especially appealing for application in WWTPs allowing to fully capture the benefits of the biogas.

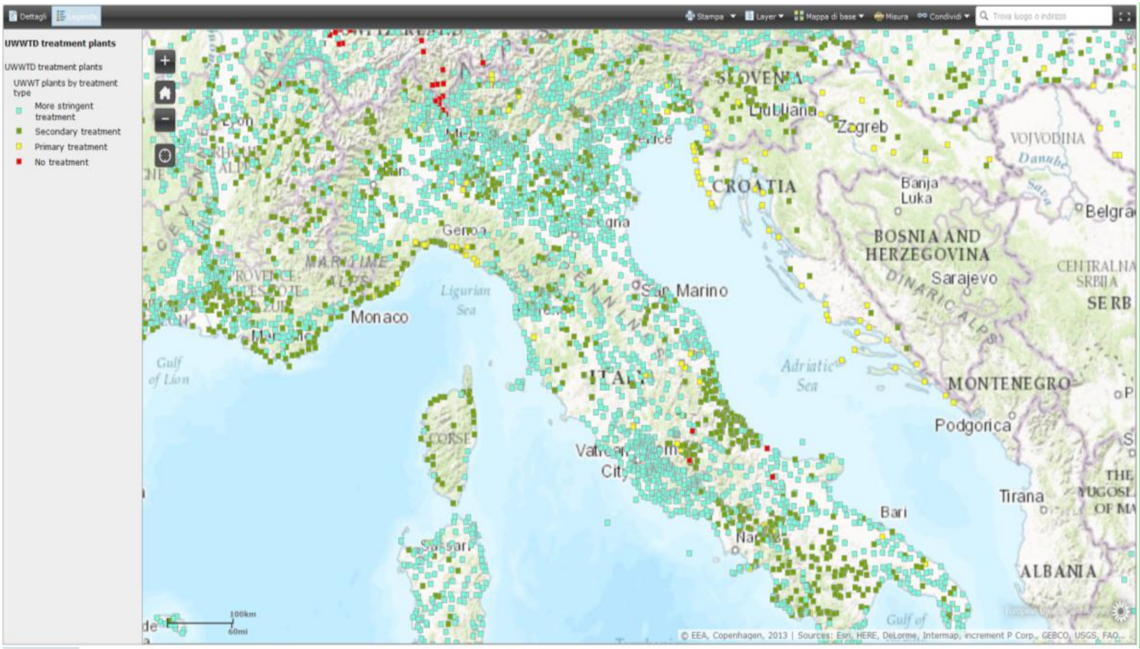


Fig. 23. WWTP Database for Europe [152]

United States

In 2016, the Pacific Northwest National Laboratory (PNNL) estimated a total of 15,014 sludge generation of publicly owned treatment works (POTW) in the U.S. [153]. These POTWs provide most of the wastewater treatment in the United States, treating 35 billion gallons of wastewater produced each day by 238.2 million Americans, or 76% of the U.S.'s population. The remainder of the population is served by decentralized or private septic [153].

Additional insights can be gained by placing the 15,014 facilities documented by PNNL into size categories based on total existing flow in millions of gallons per day (mgd) (Fig. 24). The report indicates that 23% of the U.S. population is served by 0.3% of the POTWs which comprise facilities of more than 100 mgd, 40 plants in total. A further observation indicates that 63% of the U.S. population is served by POTWs of 10 mgd-100 mgd or 3.7% of all POTWs, 522 POTWs in total [153].

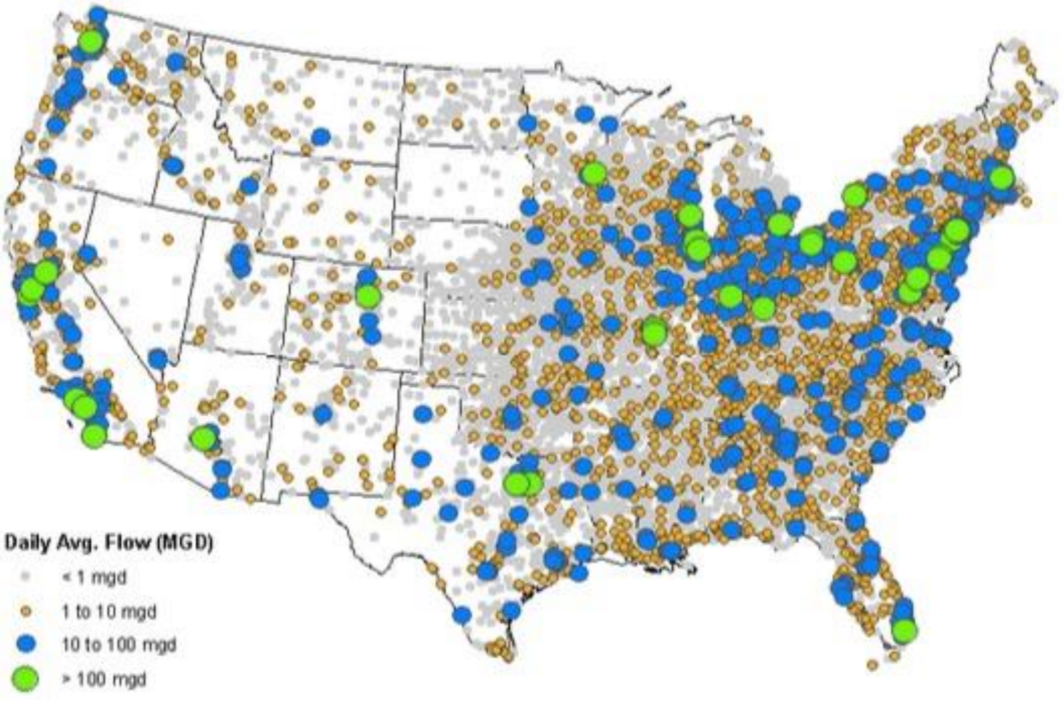
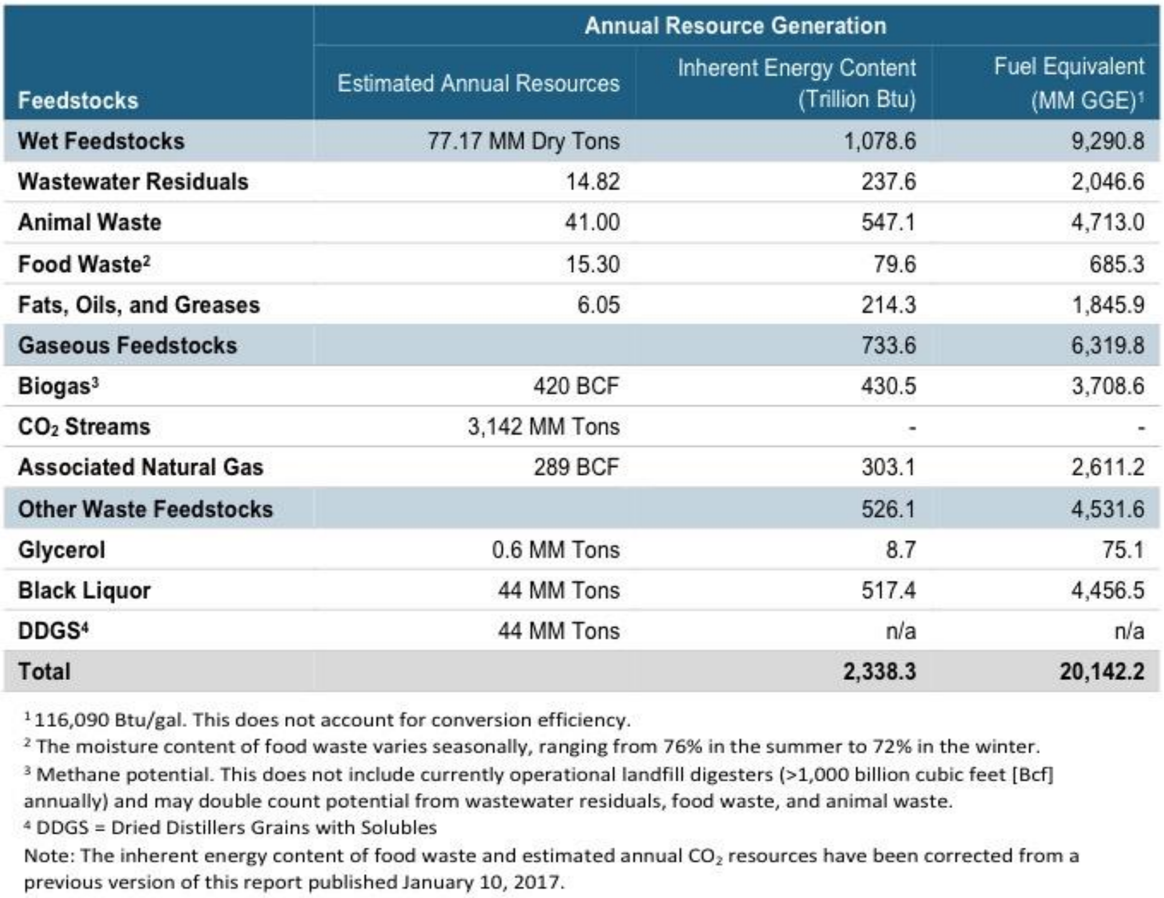


Fig. 24. Spatial distribution and influent range of 15,014 PNNL catalogued treatment plants [153]

Historically, the concept of "waste-to-energy" has referred to any of several highly mature technologies (e.g., incineration or anaerobic digestion) that decrease waste volumes. Landfill capacity scarcity, coupled with increasingly stringent disposal regulations, is necessitating novel waste management solutions. In particular, the notion that waste streams represent valuable feedstocks to produce biofuels and bioproducts is gaining currency. These feedstocks include inedible fats and greases, biogas from landfills, dairies, wastewater treatment plants, and the organic fraction of municipal solid wastes (Table 2). Conversion of these feedstocks into renewable natural gas, diesel, and aviation fuels is just beginning to gain market traction; it represents a significant opportunity for additional expansion.

Table 2. Summary of Annual Wet and Gaseous Resource Availability in U.S [153]



Feedstocks	Annual Resource Generation		
	Estimated Annual Resources	Inherent Energy Content (Trillion Btu)	Fuel Equivalent (MM GGE)[1]
Wet Feedstocks	77.17 MM Dry Tons	1,078.6	9,290.8
Wastewater Residuals	14.82	237.6	2,046.6
Animal Waste	41.00	547.1	4,713.0
Food Waste[2]	15.30	79.6	685.3
Fats, Oils, and Greases	6.05	214.3	1,845.9
Gaseous Feedstocks		733.6	6,319.8
Biogas[3]	420 BCF	430.5	3,708.6
CO_2 Streams	3,142 MM Tons	-	-
Associated Natural Gas	289 BCF	303.1	2,611.2
Other Waste Feedstocks		526.1	4,531.6
Glycerol	0.6 MM Tons	8.7	75.1
Black Liquor	44 MM Tons	517.4	4,456.5
DDGS[4]	44 MM Tons	n/a	n/a
Total		**2,338.3**	**20,142.2**

[1] 116,090 Btu/gal. This does not account for conversion efficiency.
[2] The moisture content of food waste varies seasonally, ranging from 76% in the summer to 72% in the winter.
[3] Methane potential. This does not include currently operational landfill digesters (>1,000 billion cubic feet [Bcf] annually) and may double count potential from wastewater residuals, food waste, and animal waste.
[4] DDGS = Dried Distillers Grains with Solubles
Note: The inherent energy content of food waste and estimated annual CO_2 resources have been corrected from a previous version of this report published January 10, 2017.

Terrestrial feedstocks are currently the largest resource generated for the bioeconomy, estimated at 572 million dry tons for 2017, and have traditionally constituted the primary focus of the Bioenergy Technologies Office (BETO) [154]. However, the resource assessment conducted by the National Renewable Energy Lab (NREL) and PNNL indicates that wet waste feedstocks, summarized in Table 1, could also make significant contributions to the bioeconomy and domestic energy security goals [153].

When combining the primary waste streams of interest: sludge/biosolids, animal manure, food waste, and fats, oils, and greases, a supplemental 77 million dry tons per year are generated. Of this total, 27 million dry tons is currently being beneficially used (e.g., fertilizer, biodiesel, compost), leaving 50 million dry tons available for conversion to biofuels, bioproducts or biopower. Gaseous waste streams (biogas and associated natural gas) contribute an additional 734 trillion Btu (TBtu), bringing the total energy potential of these feedstocks to over 2.3 quadrillion Btu. Additionally, these streams contain methane, the second most prevalent greenhouse gas, which constituted 12% of net U.S. emissions in 2014 according to the U.S. Environmental Protection Agency's (EPA's) greenhouse gas inventory [155] significant potential to valorize these energy dense streams while simultaneously reducing harmful emissions [153].

Wet and gaseous waste streams are widely geographically distributed, frequently in areas of high population density, affording them unique current and emerging market opportunities (Fig. 24). The size of POTWs, landfills, rendering operations, and grease collectors overlay with the largest population centers nationwide. Therefore, when compared to terrestrial feedstocks, these waste streams are largely aggregated and any derivative biofuels, bioproducts, or biopower are close to end markets [153].

At the same time, however, this proximity to populations markets often correlates with more stringent regulatory landscapes for disposal. Therefore, the value proposition presented by these waste streams commonly includes avoiding disposal costs as opposed to an independent biorefinery that requires stand-alone profitability. Aided by these and related factors, public and private entities are actively exploring and deploying novel solutions for waste stream valorization. Potential competition between biofuels, bioproducts, and other beneficial uses will likely be a key element of future markets, and clearly merits further analytical and modeling investigation [153].

While there are advantageous market and policy factors unique to these feedstocks, they are subject to significant compositional, geographic, and temporal variability. This variability creates unique challenges and requires conversion technologies that are tailored towards particular families of feedstocks. Wet and gaseous feedstocks also represent a unique set of challenges in terms of feedstock acquisition and handling. The PNNL report explores conversion possibilities for both wet and gaseous feedstocks at a wide variety of technology readiness levels. With some exceptions, the early-stage nature of many of these technologies suggests an “all-of-the-above” strategy at relatively low initial funding levels can provide an environment that encourages natural selection of solutions as they move closer to market. The U.S. Department of Energy’s Small Business Innovation Research program might be an excellent vehicle to pursue such a strategy [153].

3.5.3. Renewable energy financial schemes

The deployment of biogas projects need three elements for success: unwavering legislative structure, easy clear permitting measures, and accessibility to financing [156]. Financial entities will fund a project depending on the projected financial fulfillment compared to the project’s risks and its credit worth of the stock hold. Usually, the financial success of a biogas project depends on the availability of government financial support schemes. In some countries, it is feasible to receive financial funding for a project from public sources, low-interest loans, grants, or other assistance that encourage the roll-of renewable energy projects [157].

This study examines the inclusion of SOFC systems fueled by biogas within WWT facilities and the feasible monetary schemes that can fund the initial capital cost for the roll-out of such projects [156].

California’s Public Utilities Commission has implemented a successful financial incentive program called Self Generation Incentive Program (SGIP) [149]. This program provides financial incentives for the installation of new renewable energy technologies that are installed to meet the total eligible project cost of a facility. The program can easily be adapted to suit the deployment and development of other countries' biogas fed SOFC projects. The SGIP for FC is designed as follows: for on-site biogas projects 30 kW or larger, 50% of incentive will be received up-front; 50% will be received based on actual kWh production over the first 5 years. For projects under 30kW, 100% of the incentive will be paid up front [149] [158].

3.5.4. Methodology

The aim of the analysis presented in this section is to understand how SOFC commercialization process could start thanks to installations in a specific and selected market, such as WWTPs. By illustrating the economic costs and benefits of installing SOFCs in WWTPs, the qualitative benefits from the technology are translated into monetary value. By doing so, this analysis sheds light on the conditions under which the application of this technology becomes commercially viable. Furthermore, the implementation of a pilot case provides real-life data, which in turn reduces uncertainty related to the assumptions underlying the calculations and could, serve as an attractive reference point for other applications. As a pilot case, we consider the application of SOFCs in WWTPs in Italy (i.e., DEMOSOFC).

The analysis on the potential number of SOFCs installations in Italy has been based on the European WWTPs database from the Environmental Energy Agency (EEA) [152]. The Urban Wastewater Treatment Directive data viewer enables an easy access and analysis of the data reported under the article 15 of the Urban Wastewater Treatment Directive (UWWTD. The map (Fig. 2) reflects the most recent available information at the EU-level on implementation of the UWWTD in EU 27 based on data reported by the Member States (for reference years 2011 or 2012) in 2013. From this tool, data on directive compliance, capacity and entering load, and type of treatments, for all the WWTPs in Europe can be accessed. Data has been extracted for Italy. The information on biogas production in the listed WWTPs is not available, for this reason the analysis has been based on plants that are being defined as 'eligible' for biogas production. The eligibility depends on the plant size, in particular, on the entering load, in terms of P.E.

From internal communications with the local WWTP's owner [159], the minimum plant size for biogas production has been defined, 20,000 P.E., confirmed also by literature sources [160], [161]. The main reason for this limit is linked to economic profitability of anaerobic digestion: fixed cost related to this technology are quite high and make the overall investment not competitive under a certain size. The value is varying between country to country and is depending on the technology learning and cost reduction for anaerobic digestion, even if it is a commercial product. For this study, a reference number has been chosen and kept constants for all the analyses.

In Italy, 5,672 WWTPs are presented in the database, but only 83.5% of them shows related data on entering load and/or capacity. Among the total plants, 670 shows an entering load ≥ 20,000

P.E., corresponding to 11.85% of the total plants. These numbers confirm the distribution of WWTPs in Italy by size of a high number of small-medium size plants. All WWTPs in Italy have an average entering load of 12,324 P.E., hence making it lower than the mandatory limit.

The ‘eligible’ 670 plants are the ones considered for biogas production and consequently for SOFCs systems installation. The analysis has been first developed for a ‘base case’ scenario, followed by other studies to show the influence of different parameters. The methodology for calculating the SOFC power installed for each plant is presented below:

1) Calculation of the biogas potential production in the WWTP. Starting from the entering load for each plant (in P.E.), the potential biogas production can be determined by means of the biogas production rate, expressed in liters of biogas produced per P.E. per day. This number is strongly changing from plant to plant, depending on the technology and the process management involved in the sludge line. For this reason, a base value of 15 L biogas/ P.E./ day (Table 2), referred to the local SMAT Collegno WWTP (see DEMOSOFC project website for more information [149]), was chosen as starting value. Higher productivity rates can be reached and are already measured in other WWTPs.

2) Calculation of the biogas Lower Heating Value (LHV). From the biogas potential production, the methane content should be used to calculate the inlet power (in terms of LHV) contained in biogas. The analysis, for all the case studies, has been performed using a fixed 60% methane content.

3) Calculation of the SOFC power installed. The available fuel (biogas) is used for electricity production by means of an SOFC system. By knowing the amount of biogas available in each plant and the efficiency of the SOFC’s system, it is possible to calculate the maximum amount of power, which can be produced from that fuel using that technology.

Table 3. Input parameters for the base case scenario.

Parameter	Value	Unit
Minimum plant size for biogas production	20,000	P.E.
Biogas production rate	15	L biogas/ P.E. / day
Methane content in biogas	60	%
SOFC electrical efficiency (target)	60	%

This procedure has been repeated for all the ‘eligible’ WWTPs. The potential SOFC installed power is consequently determined, starting from the biogas power by means of the SOFC electrical efficiency. Industrial size SOFC systems currently show efficiency higher than 55%. The efficiency has been fixed to a target value (60%) for the base case and varied in the other scenario (Table 3).

By means of the presented methodology, the total number of SOFCs installed has been determined. The minimum plant size, 20,000 P.E., in the base case scenario, corresponds to a SOFC system of 45-kW electrical. This size has also been considered as the standard SOFC module size and results, when expressed in number of units, are always referred to a 45-kW electrical SOFC module.

Table 3 shows the other investigated scenarios for what concerning biogas production rate and SOFC efficiency. Scenarios are linked to the variability of two parameters:

- Biogas production rate. The specific biogas production yield is strongly varying from plant to plant. It can be influence by external temperature, by pre-treatments on the inlet biomass to the anaerobic digester, by the quality of the inlet wastewater and many other factors. For this reason, different values have been analyzed, starting from 10 L biogas/PE/day and reaching a target value of 40 L biogas/PE/day.
- SOFC electrical efficiency. Current SOFC efficiency is 53% [162] in the framework of the DEMOSOFC project, where an industrial size SOFC will be installed in a local WWTP. Nevertheless, there are commercially available systems, which currently show lower performance, and other advanced SOFC, which are reaching (or have already reached) a 60% efficiency from fuel to AC power. For this reason, a variation of this parameter has been also considered from 50 to 60%.

Table 4. Case studies definition, in relation to Biogas production rate and SOFC electrical efficiency

		Base Case	**Worst Case**	**Current Case**	**Target Case**
Biogas production rate	L biogas/PE/day	15	10	25	40
SOFC electrical efficiency	%	60	50	55	60

By crossing the variation range of these two parameters, the three scenarios have been identified (Table 4). Starting from the number of units that could be delivered by a company producing SOFCs in a WWTPs sector in Italy (670 installations), to finally understanding the range of the potential decisive price driving the WWTP's market supply in Italy.

3.5.5. Evaluation of the SOFC system annual costs at different production volumes

In order to evaluate the number of units that should be ameliorated (from an economic point of view) to drive the SOFC stationary market by means of an incentive program, a simple economic evaluation has been performed.

The analysis has been done on the evaluation of plant annual savings calculated as the difference between the plant costs (investment and operation costs) and the revenues linked with the savings in electricity bought from the grid. The evaluation is shown for a 45-kW system, corresponding to one

SOFC unit. The same concept could be applied to larger installations. The annual costs have been evaluated for different SOFC production volumes related costs (Fig. 4 and Fig. 5) and a trend for the annual savings at different production volumes level has been calculated.

Assumption and input data for this analysis are:

- Time period on which the analysis is performed: 10 years
- Capacity factor of the system: 95%
- Cost of electricity: initially assumed 15 c€/kWh as in the DEMOSOFC real case study, but then varied between 5 and 20 c€/kWh.
- SOFC system size: 45 kW electrical
- Clean-up cost: equal to the LCOE's calculation (1,000 €/kW investment cost and 1c€/kWh operating cost)
- Cost for the plant preparation and system installation: equal to the LCOE's calculation (1,500 €/kW)

The annual cost has been determined as the sum of the investment cost – spread over the chosen time period – and the operating cost. The annual revenues are related to the savings in electricity thanks to the CHP installation. The difference among these two values is the annual savings which can be negative (plant is losing money) or positive (plant saving/earning money).

Results are shown in Fig. 25 for different production volumes. The total costs are shown with the red line; revenues with the green line; and the difference (savings) with the blue line. As shown, savings start to be positive from 191 units produced (8.6 MW), however, when the Italian WWTP's potential number of installations reaches 2,497 units, an annual saving of 21,541 € is generated based on the installation of 45 kW SOFC-based CHP plant.

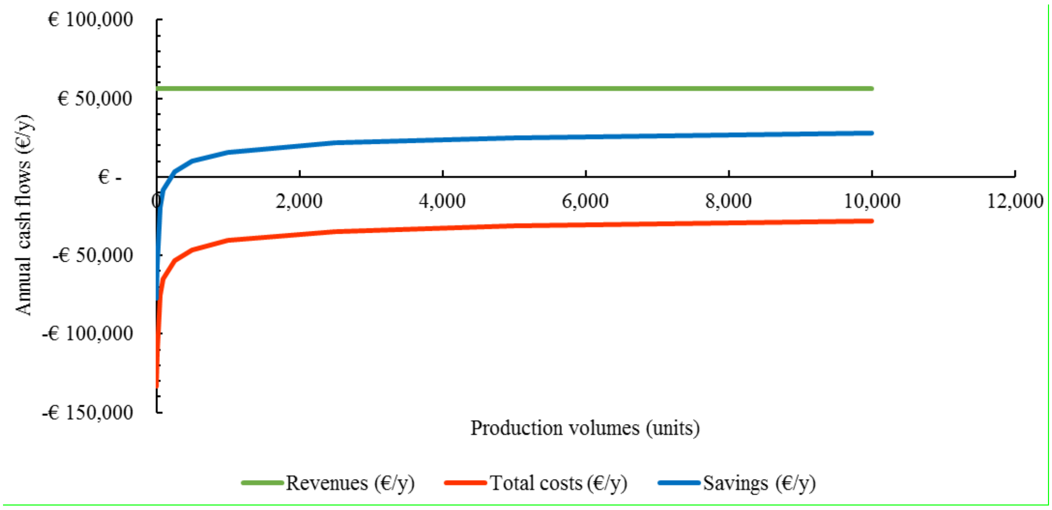


Fig. 25. Results for the annual costs evaluation for different units produced.

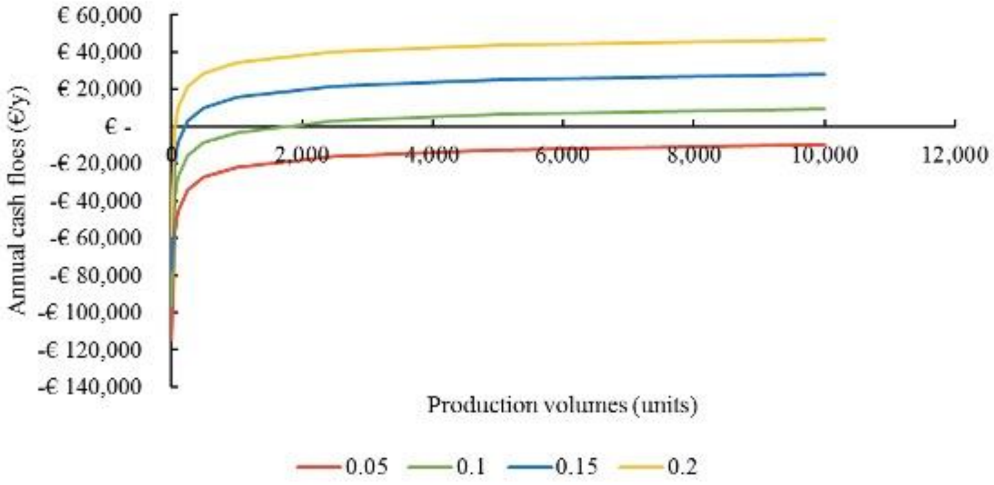


Fig. 26. Sensitivity analysis on influence of electricity price (in €/kWh) on annual savings

Since prices of electricity fluctuate depending on the country, production plant, plant size, and the overall electricity purchased (yearly) from the grid, a sensitivity analysis reliant on these values is proposed, with results for 5, 10, 15 and 20 c€/kWh electricity price. Savings are shown in Fig. 5

The price of electricity strongly influences the break-even point among costs and revenues, since revenues are proportional to the cost of electricity (Fig. 26). For the lowest energy price (5 c€/kWh), break-even is never reached between costs and revenues, meaning that SOFCs are not yet commercially suitable for markets where electricity price is very low; in these areas, an important driver for SOFCs commercialization could be the environmental advantages SOFCs are offering.

With a 10 c€/kWh electricity price, the break-even point is reached at 1564th unit produced (70.4 MW), alongside a SOFC investment cost of 3,452 €/kW. The break-even point shifts downward at 191 units produced at the 15 c€/kWh electricity price scenario. In the aforementioned SOFCs' investment cost the system starts to be profitable at 6,420 €/kW.

Finally, in the high electricity price scenario (20 c€/kWh), SOFCs start generating income (10-year period) after the 52nd unit is produced (2.3 MW). The break-even point related SOFC cost is 9,404 €/kW.

A final analysis is conducted when the break-even point (SOFC installation investment has a positive value) starts generating savings for the plant (10 yrs.). Therefore, the actual break-even point is reached when the minimum number of units need to be subsidies by an incentive program. Further analyses should be devoted to the understanding of the competitiveness of the SOFCs solution compared to the traditional systems for biogas exploitation such as ICE and micro-turbines. A fully market entry of the technology will be reached when annual savings are not only positive but also greater than the competition.

3.5.6. Results

The economic profile of a SOFCs installation, assuming today’s costs, is not profitable from investment point of view. For this reason, policies and subsidies should be considered to support a certain portion of the 670 installations, until a competitive cost is reached.

In the analysis of the ‘base case’ scenario, the following results have been obtained:

- 112 MWs can be installed in Italy considering a standard SOFC module size of 45 kW for 2,497 units.
- The installation of 2,497 units could lead to a robust reduction in SOFC’s price.
- Investment cost: 3,007 €/kW (-83% with respect to the current scenario).
- Stack replacement cost: 549 €/kW/replacement (-79.7% with respect to the current scenario).
- Maintenance cost: 2,508 €/yr. (-58% with respect to the current scenario).
- Number of replacements during a lifetime (20 yrs.): 2.92

This scenario generates an LCOE (assuming the same current cost for the clean-up unit) equal to 5.95 c€/kWh, nearly 70% lower than the current scenario.

The SOFCs installation in WWTPs has been considered as a potential driver to reduce the fuel cell specific cost. The current SOFC cost scenario (Fig. 27) investment cost higher than 17,000 €/kW, a stack replacement cost of 2,710 €/kW/replacement, and a maintenance cost of 6,000 €/y. With this input data and the current cost for biogas cleanup system (investment cost 1,000 €/kW and maintenance cost 1 c€/kWh [163]), the LCOE of the SOFCs installation in a 20 year period is equal to 19.56 c€/kWh, considerably higher than the current price of electricity for typical user in Italy [164].

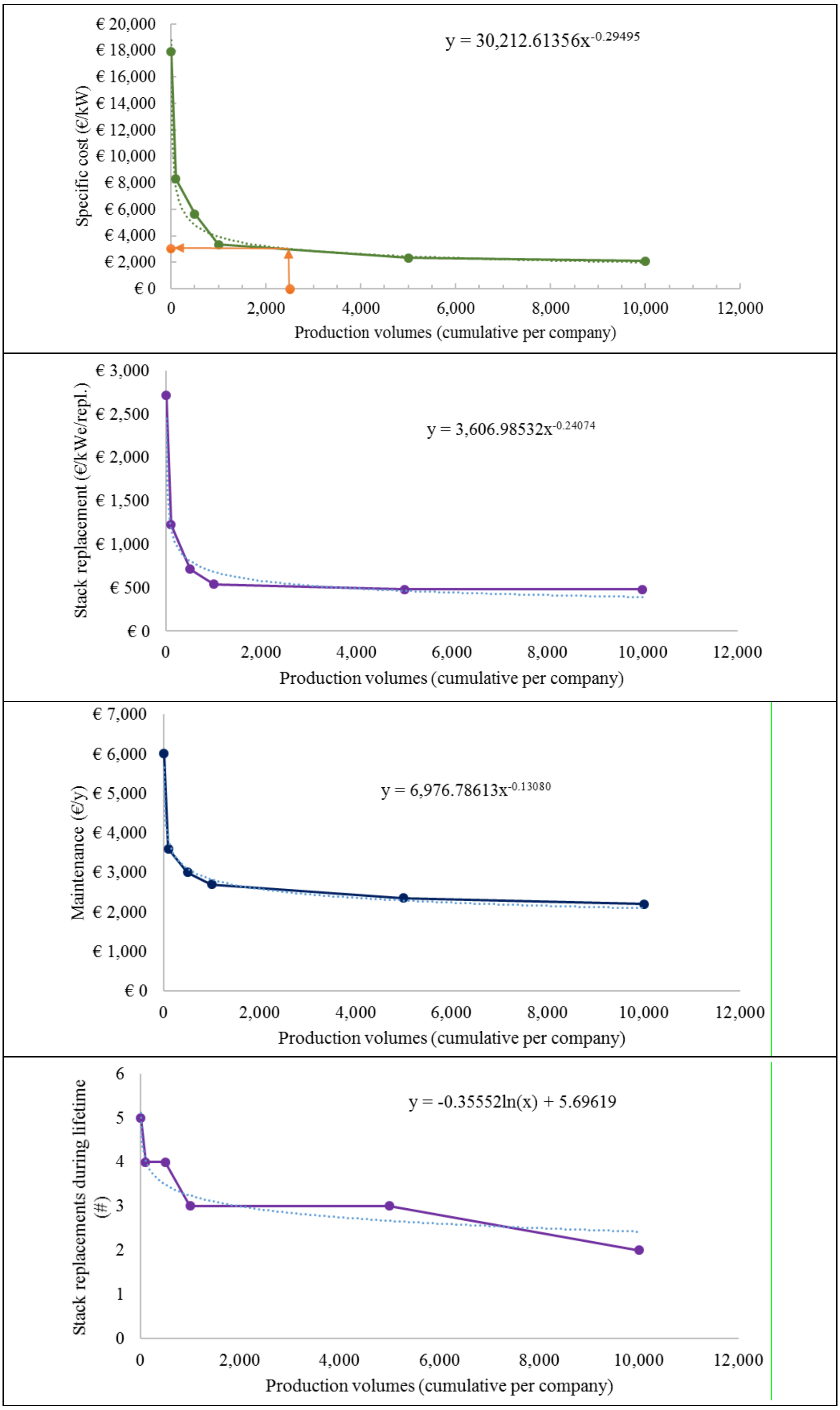


Fig. 27. Learning curves for SOFC specific investment cost, stack replacement cost and maintenance cost [165]

Results for the sensitivity analysis are shown in Fig. 28. Biogas production rate has a strong influence on the number of installations, together with the SOFC's efficiency. Number of potential MWs to be installed varied from 55 (worst case scenario) to 318 (target scenario). Despite the high variation in terms of MWs and units installed, the 'final' SOFC's investment cost is less variable, ranging from 2,212 to 3,707 €/kW (Fig. 5). This is due to the exponential trend of the learning curve (Figure 27): the curve displays a strong cost reduction up to 1,000 units and then the trend slowly reduces to a target value of around 2,000 €/kW. In all the analyzed scenarios, even the worst case, the potential number of SOFCs installation is higher than 1,000 units, therefore, the resulting SOFC cost shows less variations compared to the volumes.

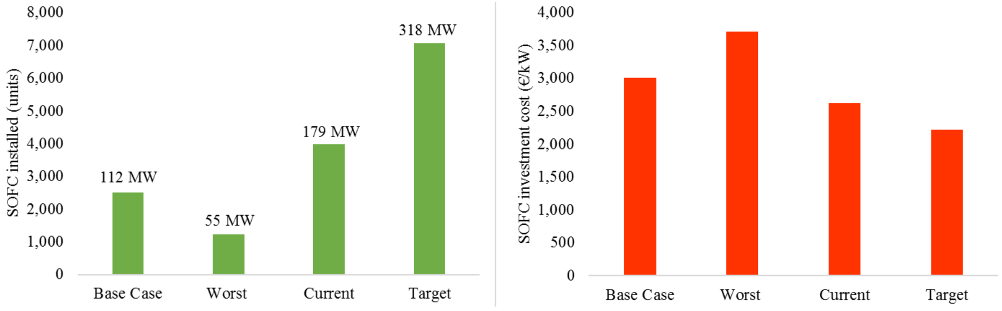


Fig. 28. SOFC installations and final investment cost for the different scenarios.

Power-to-Fuel Through CO_2 Reutilization & High-Temperature Electrolysis Technical and Economical Comparison Between Synthetic Methanol and Methane

This chapter presents some pathways to alternative mid- to long-term CCU options, specifically, the capture and transformation of CO_2, to produce sustainable, synthetic hydrocarbon or carbonaceous fuels, mainly for the transportation industry.

Power-to-X technologies are considered to play a significant role in the CCU paradigms. They convert electricity from renewable energy into hydrogen, methane or liquid fuels which are then utilized to drive climate-neutral vehicles. This renewable fuels could also substitute the fossil fuels used in relation to heat supply [166]

Most of the infrastructures serving the transport industry mainly relies on petrol, heavy fuel oil, and kerosene and this is likely to stay unchanged as a transitional period is sustained over many years to come, especially in some applications such as the aviation industry. One solution could be to use chemical processes to convert electricity into gas or liquid fuels, which are referred to as e-fuels. These e-fuels can then be used in the transportation industry (e.g., to power cars, trucks, and airplanes). These renewable fuels (produced from renewable electricity) could substitute fossil fuels not only in the transport industry, but also it can be used for heating and industrial purposes.

The term ‘Power-to-X’ includes all procedures that convert electricity, (i.e., power) into other energy vectors X [167]. In order to get the big picture, energy supply needs to be observed from an integrated perspective, instead of considering electricity generation, transport, and industry separately; therefore, innovations are crucial for the development of a new paradigm.

Considering the expected growth of renewable energy, many studies see great potential for Power-to-X technology; however, aside from a few exceptions, there are currently only few marketable options. The problem is that manufacturing costs are still too high, therefore investors usually favor fossil fuels since the resources are readily available, and they are less expensive.

In other words, in order to commercialize synthetic fuels, the approach has to revolve around the concept of the large-scale CCU, and how this challenging approach could assume an important role in undertaking the issue of global CO_2 emissions.

E-fuels can be considered as part of the energy transition. There are three main possible strategies (among others) involving CO_2 conversion by physicochemical approaches: sustainable (or renewable) synthetic methanol, synthetic methane production derived from the CO_2 recovered from the flue gases expelled from coal, gas, or oil-fired electric power stations, and photochemical production of synthetic fuels [167]. Although these three archetypal areas vary in their final applications, the underline thermodynamic considerations revolve around the conversion process: hence the utilization of CO_2. Also, the CO_2 captured from flue gases need to be considered as a transitory solution, because the final goal is to capture CO_2 directly from the air in order to determine the effect of perfect carbon equilibrium.

Among the possible E-fuels, the focus was geared towards the analysis on e-methane (a gas-form e-fuel) and e-methanol (a liquid-form e-fuel). In both cases the process consists of mixing hydrogen produced by electrolysis (power to hydrogen) with CO_2 in order to achieve hydrogenation synthesis via a catalytic reactor.

An energy analysis is then performed, with special consideration to the thermal integration (minimization of external heat requirements) via pinch analysis, as well as a final estimation of power-to-fuel overall efficiency. The study demonstrates that power-to-methane and power-to-methanol process can achieve efficiency of up to ≈ 77% and ≈ 59%, respectively. The energy analysis (based on the process modeling developed for both the systems) and the heat exchange network design enabled the development of capital expenditure estimation.

An economic analysis comparison for the production cost of both synthetic fuels was performed with the purpose of highlighting any potential risk related with the systems. The economic analysis considered the effect on synthetic fuel cost of some parameters as electrolysis specific costs, the expenditure for carbon dioxide, electricity price, and yearly operating hours (capacity factor of the plant). In the work, we have concentrated the analysis on the technological option of high temperature solid oxide electrolyzer (SOEC), because of its higher electrical efficiency and its potential to have a positive thermal integration with other sections of the entire transformation chain. The results show that for both systems the SOEC electrolyzer is the greatest capital expenditure of the design. Methanol synthesis plant showed lower efficiency and higher investment costs; on the other hand, fossil-based methanol has higher costs ($/MWh) than fossil methane; thus, the breakeven point of electricity price (i.e., that making economically comparable synthetic and fossil fuel) is similar for the two considered cases.

It was concluded that, to produce an economically attractive market for e-methane and e-methanol, the production plants should maintain a utilization factor of approximately 50%, the cost of SOECs should be near to 1050 €/kW and the electricity required to run the system needs to be supplied from renewable sources at a very low cost (below 40-50 $/MWh).

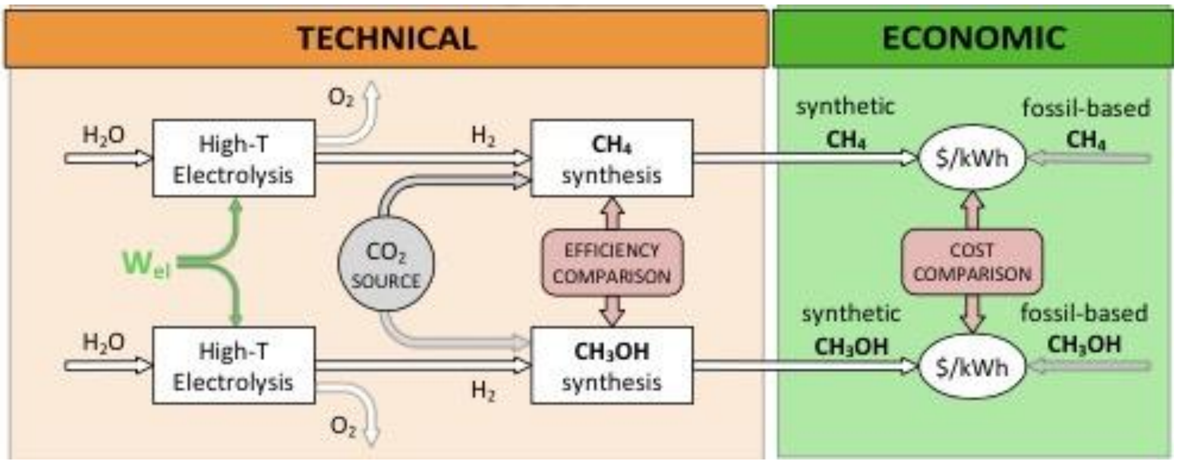


Fig. 29. Technical and economic layout of the production of synthetic fuels (methane and methanol)

Figure 29 is a graphical overview of the two chemical processes used to synthesize methane and methanol from CO_2, H_2O and the use of renewable energy. The goal is the compare the efficiency between the two processes when producing both e-fuels. The graph also depicts the economic analysis by comparing synthetic vs. fossil-based methane and methanol. Finally, a cost comparison is conducted in order to determine which of the two e-fuels would be the most economically attractive to investor's bottom line when compared to fossil fuel alternatives.

CO_2 capture and CO_2 neutral fuels

CO_2 neutral fuels are synthetic hydrocarbons produced from recycled carbon dioxide and water (Fig. 30). These molecules are split and subsequently synthesized into fuels by employing renewable energy such as wind and solar energy. After synthetic fuel combustion process, the CO_2 emitted is recycled (Fig. 31). This CO_2 is captured from point source initially, but eventually must include direct air capture to account for emission from inherently dispersed source such as petrol-driven motor cars, airplanes and gas-fired household appliances. By recapturing and re-using the CO_2 emitted, the CO_2 cycle is closed, establishing an equilibrium condition.

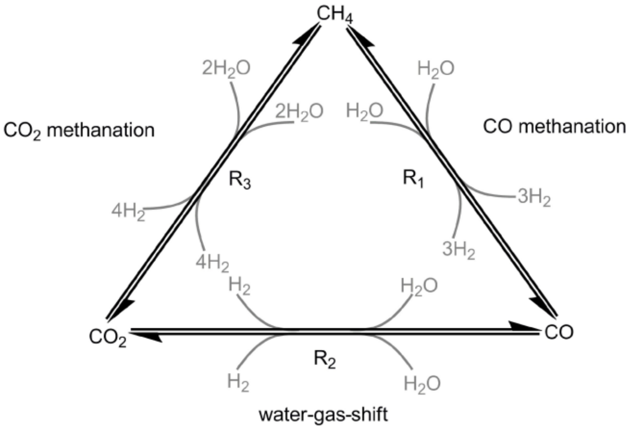


Fig. 30. CO_2 utilization diagram [168]

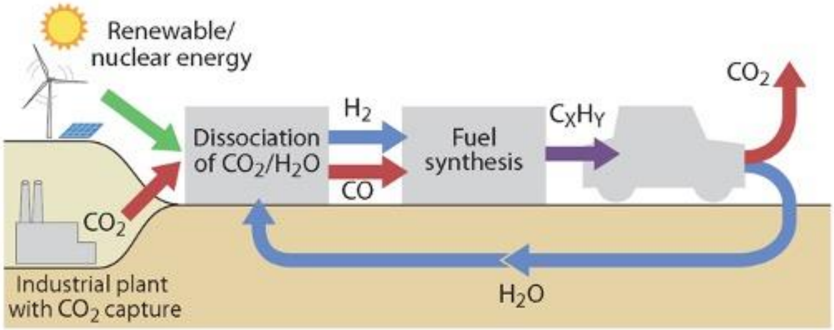


Fig. 31. CO_2 recycled synthetic fuel cycles [169]

The conversion of carbon dioxide into fuels and chemicals permits for the displacement of fossil-based compounds used in the chemical, transport, power production, pharmaceutical sectors. Nowadays there are different commercial technologies to capture carbon dioxide from energy production processes. Three technology routes are currently most intensively discussed: CO_2-capture from the flue gas stream after combustion (post-combustion), the use of nearly pure oxygen for fuel combustion instead of air which increases the CO_2-concentration of the flue gas (Oxy-fuel) or the CO_2-capture from the reformed synthesis gas of an upstream gasification unit (Pre-combustion) [170].

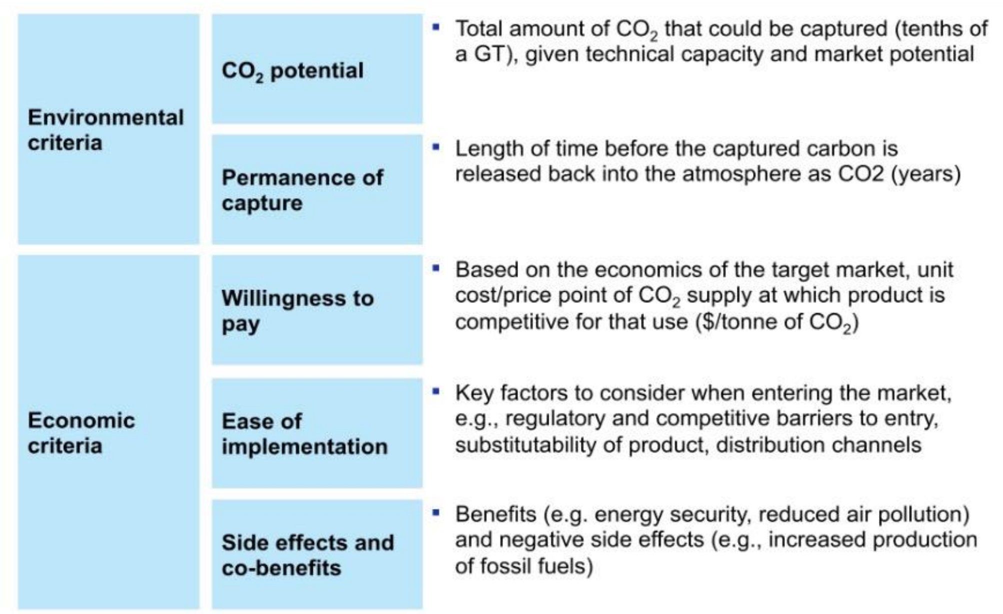
Integrated gasification combined cycle (IGCC) and oxy-coal combustion (OCC) are promising alternatives for CO_2-free power generation. IGCC plants integrated with CCS are more affordable, due to integration with the more effective CO_2 pre-combustion capture technology, with an energy penalty of about 7–10 percentage points. Also, oxy-fuel combustion can be an interesting solution for CO_2-free power generation from coal and other fossil fuels, involving a flue gas mainly composed by CO_2 and water vapor, which can be easily separated [171].

When considering cost, the oxy-fuel combustion could reach better results: for example, in a cement production the oxy-fuel leads to achieve an increase of the 32% of the production cost (with respect to the 102% of increase for the post combustion capture). The lower CO_2 avoidance cost is represented by oxy- fuel option with 55 € per ton of avoided CO_2 [66]. Carbon dioxide conversion into syngas has been recently studied to reduce emissions and improve the efficiency of coal gasification processes [172].

E-fuels-related technologies

The Global CO_2 Initiative (GCI) led a market assessment by applying five key criteria CO_2 potential, permanence of capture, willingness to pay, ease of implementation, side effects and co-benefits), both economic and environmental to assess CO_2-based products (Table 5) [56]. GCI based its conclusion on a five-year research that was completed in early 2016.

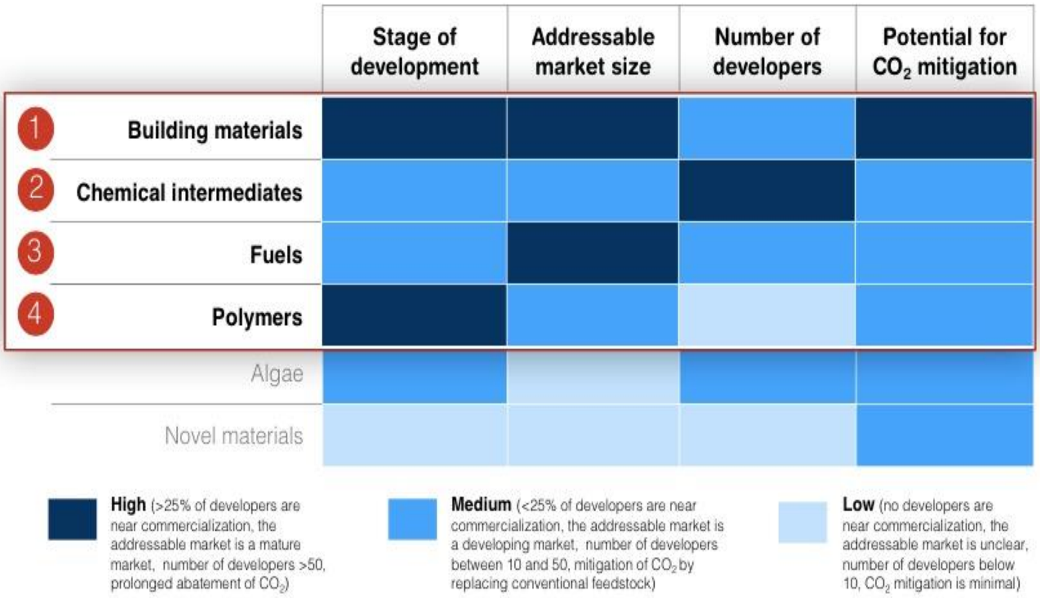
Table 5. Market Assessment: Criterial for selecting technologies [11]



Environmental criteria	**CO_2 potential**	- Total amount of CO_2 that could be captured (tenths of a GT), given technical capacity and market potential
	Permanence of capture	- Length of time before the captured carbon is released back into the atmosphere as CO2 (years)
Economic criteria	**Willingness to pay**	- Based on the economics of the target market, unit cost/price point of CO_2 supply at which product is competitive for that use (\$/tonne of CO_2)
	Ease of implementation	- Key factors to consider when entering the market, e.g., regulatory and competitive barriers to entry, substitutability of product, distribution channels
	Side effects and co-benefits	- Benefits (e.g. energy security, reduced air pollution) and negative side effects (e.g., increased production of fossil fuels)

The detailed market assessment study found that carbon utilization has the potential to reduce carbon emissions over 10% by 2030 [56].

The study analyzed the current state of CO_2 utilization, assessing almost 180 global technology developers based on their stage of development, addressable market size, number of developers, and potential for CO_2 mitigation. Momentum is favorable for four major markets: building materials, chemical intermediates, fuels, and polymers (Fig. 32) [11].



	Stage of development	Addressable market size	Number of developers	Potential for CO_2 mitigation
① Building materials	■	■	▨	■
② Chemical intermediates	▨	▨	■	▨
③ Fuels	▨	■	▨	▨
④ Polymers	■	▨	□	▨
Algae	▨	□	▨	▨
Novel materials	□	□	□	▨

■ **High** (>25% of developers are near commercialization, the addressable market is a mature market, number of developers >50, prolonged abatement of CO_2)

▨ **Medium** (<25% of developers are near commercialization, the addressable market is a developing market, number of developers between 10 and 50, mitigation of CO_2 by replacing conventional feedstock)

□ **Low** (no developers are near commercialization, the addressable market is unclear, number of developers below 10, CO_2 mitigation is minimal)

Fig. 32. Market Assessment: Top 4 markets in terms of environmental impact and commercial opportunity [11]

Even though the manufacturing of polymers through CCU technologies is not yet economically favorable, other CCU technologies, such as mineral carbonation and concrete curing for the development of building materials, are currently readily scalable and partially commercialized [11]. According to GCI’s research, the markets for fuels and chemical intermediates (e.g., methanol and methane), present the broadest areas of market applications.

Methane is mostly used in three key sectors: transportation, electricity production and civil heating sector [173]. Furthermore, due to the gradual global outspread of the creation and advancement of clean electricity policies, methane can play a fundamental role in the near future. This is especially the case when considering the substitution of fossil methane with renewable methane, in the form of bio-methane and synthetic methane (which is the analysis conducted in this study).

Methanol production is one of the most effective and mature CCU routes. Syngas is converted into methanol by the exothermic reaction (Eq.1):

$$\mathrm{CO} + 2\mathrm{H}_{2(g)} \rightarrow \mathrm{CH_3OH}, \quad \left(\Delta \mathrm{H}^0_{298K} = -91.0\,\frac{\mathrm{kJ}}{\mathrm{mol}}\right) \qquad \text{(Eq.1)}$$

Methanol can already be used as substitute fuel in internal combustion engines (ICE)-powered cars (including hybrid cars and plug in models) with minor modifications to existing engines and fuel systems [94]. Methanol can also be used to produce dimethyl ether (DME) via its dehydration or employed as a reagent for transesterification reactions in biodiesel production [174]. Several studies have focused on methanol synthesis, e.g., integrated with enhanced gas recovery [175] or biogas production [176]. Under normal conditions, methanol is a liquid that permits for easy storage, transportation, and distribution, a similar process used with gasoline and diesel fuel.

To sum up, methanol production is one of the most effective and mature CCU routes with hydrogenation of CO_2 because it can be considered a commodity chemical (not only DME, but also ethylene, and propylene, two chemicals produced in large amounts by the petrochemical industry) [38].

It is worth noticing that both methane and methanol, can also be utilized in fuel cells to produce electricity; either directly [177][178] or indirectly, after an external reforming process converting the fuel into hydrogen and carbon monoxide [179][180].

The main energy input for these conversion technologies is usually considered as renewable. This is an important requirement for these technologies, the primary energy input needs to have a low CO_2 emissions intensity to have a positive balance of CO_2 reduction in the whole process.

In the renewable source domain, the largest exponents are currently solar, wind, and hydropower. However, the progressive dispersal of renewable energy has caused some issues related to the energy system management due to the natural intermittency of renewable energy sources (RES). Over the last twenty years RES has grown at an average annual rate of 2.2%; solar and wind power penetration increased with average annual rates of 46.2 and 24.3%, respectively [181]. In this context, the need of effectual management in the face of the increasing amount of RES-based electricity can be confronted in various ways, most likely also considering solutions based on power-to-gas and power-to-liquid technologies; through these technologies it is feasible to store power directly into an existing infrastructure (e.g., the gas network) evading the waste of RES or its limitations. In fact, thanks to power-to-fuel paradigms, RES development can also meet non-electric energy needs such as fuels for transportation and industry feedstock, which currently rely on fossil fuels. Therefore, the conversion of surplus renewable electricity into a more appropriate chemical feedstock (power-to-liquid and power-to-gas) could help offset RES intermittency while delivering a diverse mix of energy carriers. If recycled CO_2 is used in the fuel synthesis process, consequently, the overall emissions reduction will follow [182].

In the power-to-fuel pathway, low-cost surplus electricity is used to feed the electrolysers that generate hydrogen (H_2) from water. The subsequent catalytic reaction between H_2 and CO_2 allows the production of gaseous methane or liquid methanol. Focusing on electrolysis, two low-temperature technologies are available: alkaline and proton exchange membrane (PEM) electrolyzer operating in the range 60-90 °C and 40-80 °C, respectively [183]. However, a more encouraging technology (in terms of conversion efficiency) is the one that incorporates solid oxide electrolysis cells (SOEC): the operating temperature (700–900 °C) of this device is higher than the technologies mentioned above [184]. High-temperature solid oxide electrolysis system can achieve better results of a PEM system (energy efficiency until 14% higher, reaching a maximum efficiency of 75.9%) working at high hydrogen production rates (i.e., high current density) [182].

Nevertheless, the deployment and commercialization of new technologies developed to produce synthetic fuels must be economically appealing to investors, especially if compared to current prices of fossil derived commodities. To generate an attractive market, it is vital to advance and apply certain facets of the development of the synthetic fuels production, for example: reducing the cost of certain electrolysis technologies and using of the electricity input in periods of low market prices of the commodity.

In this context, the goal is to compare two different types of production plants designed to produce methane and methanol through the process of high-temperature electrolysis carried out by solid oxide electrolysers (SOEC). The first plant is based on the coupling between steam electrolysis and two catalytic reactors fed with a stoichiometric mixture of hydrogen and carbon dioxide (H_2/CO_2 molar ratio of 4) slightly diluted with unreacted steam. The resulting chemical reaction allows the production of a synthesis gas with high methane content. The second plant differs from the first one for the reactor section: the H_2-CO_2-H_2O mixture feeds a high-pressure catalytic reactor where methanol, water and carbon monoxide are formed. A subsequent distillation allows to separate the methanol from the other by-products. Energy analysis has been carried out to evaluate the power-to-fuel overall efficiency, while economic analysis enabled the comparison between synthetic and fossil-based (conventional) fuels. The analysis of the two concepts allowed to underline potential and drawbacks related to the considered processes and technologies. If compared to other previous studies [185] [186], in this analysis a comparison between SOEC-based methanol and methane is carried out, both from an energy and economic standpoint. The comparison highlights the dissimilarities in terms of process design, overall power-to- fuel efficiency and synthetic fuel production cost (including its sensitivity to CO_2, electricity and SOEC price).

Methodology

4.3.1. Methane production

The synthesis of methane can be done exploiting the reaction between anthropogenic carbon dioxide and renewable hydrogen (Fig. 33). Under exothermic reaction (Eq.2), the hydrogenation of CO_2 produces methane and water as by-products (Sabatier reaction).

$$\mathrm{CO_{2(g)} + 4H_{2(g)} \leftrightarrow CH_4 + 2H_2O_{(g)}} \qquad (\Delta \mathrm{H}^0_{298\mathrm{K}} = -165.0\,\frac{\mathrm{kJ}}{\mathrm{mol}}) \qquad \text{(Eq.2)}$$

The operating temperatures are generally slightly higher than to produce methanol (250-400°C) at similar pressure values. Several metals such as Ni, Ru, Rh, and Co may be used as the catalyst for the methanation reaction. Ni-based catalysts represent a good compromise due to relatively high activity, suitable CH_4 selectivity, and low raw material price [187]. The catalysts in this case are generally Ni-, Rh- or Ru-based [40]

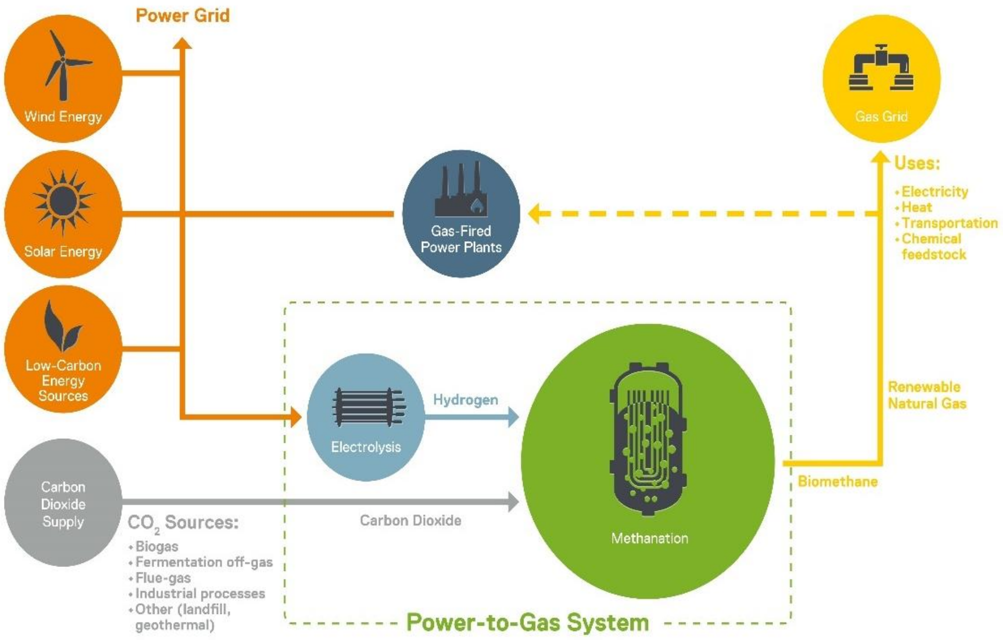


Fig. 33. Synthetic methane production overview [188]

The equilibrium of the reaction is influenced by pressure and temperature; in thermodynamic equilibrium and high pressure favors the production of methane; however, high temperature limits methane formation. Catalytic methanation reactors are usually operated at temperatures between 200°C and 600°C and at pressures ranging from 1 to 100 bar. As previously mentioned, methanation reaction is highly exothermic; consequently, this presents a major problem because a methanation reactor must have suitable temperature control to prevent thermodynamic limitation and catalyst sintering [189]. In large-scale industrial applications and for continuous operations, the temperature control is attained with a series of adiabatic fixed-bed reactors and intercooling of the stream between each reactor. However, power-to-gas processes are implemented at smaller scales, with intermittent operations, for which adiabatic reactors are not suitable. In this context, isothermal reactors where a cooling fluid directly chills the reacting mixture are usually preferred. Other types of reactors such as fluidized bed reactors, three-phase reactors or structured reactors are also being researched, however these technologies are still in the development phase [190]. By rising the allowable temperatures for methanation catalysts, methane synthesis can be performed by a once-through method in quasi-isothermal reactors cooled by evaporating water which generates saturated steam. Under favorable conditions, such systems may produce a synthetic natural gas (SNG) with methane content above 90 mol.-% in only one catalytic step [191].

4.3.2. Methanol production

Methanol can be produced from CO_2 in two different ways: in one step or in two steps. The one step conversion is the direct hydrogenation of CO_2 to methanol. The two-step conversion reduces CO_2 into CO by breaking the carbon dioxide C=O bond through the reverse water gas shift (RWGS) reaction, and then into methanol by the reaction between CO and H_2. In this analysis, the conversion of CO_2 in one step was employed. Some routes of conversion of CO_2 to produce fuels are shown in the following Figure 34.

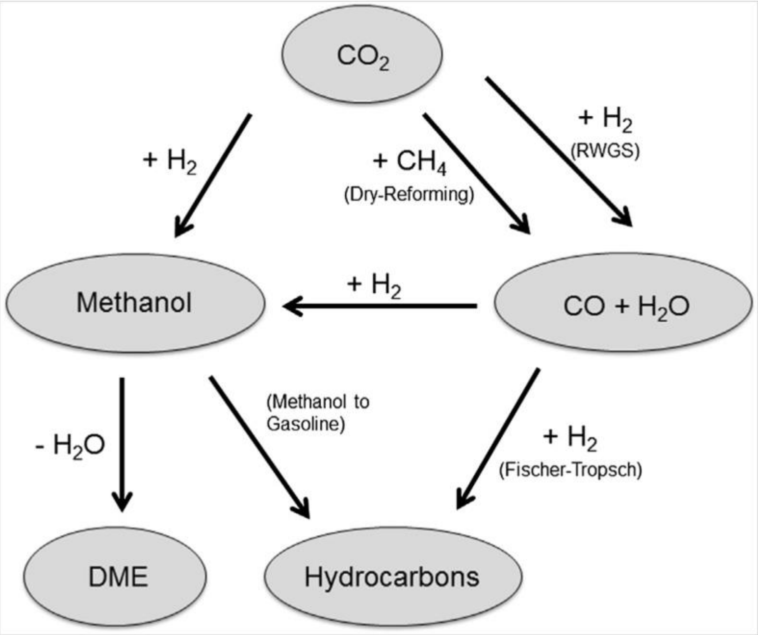


Fig. 34. CO_2 utilization diagram [186]

Exothermal reactions (3) and (4) allow the production of methanol starting from hydrogen and CO or CO_2, respectively. The RWGS reaction (5) occurs in parallel [192].

$$CO(g) + 2H_{2(g)} \rightarrow CH_3OH(l) \quad (\Delta H^0_{298K} = -128.0\,\frac{kJ}{mol}) \qquad (Eq.3)$$

$$CO_2(g) + 3H_{2(g)} \rightarrow CH_3OH(l) \quad \left(\Delta H^0_{298K} = -87.0\,\frac{kJ}{mol}\right) \qquad (Eq.4)$$

$$CO_2(g) + H_{2(g)} \rightarrow CO_{(g)} + H_2O(g) \quad \left(\Delta H^0_{298K} = +41.0\,\frac{kJ}{mol}\right) \qquad (Eq.5)$$

RWGS and one of the two hydrogenation reactions are enough to completely describe the system. Methanol synthesis is exothermic and involves a decreasing number of moles, thus it is favored at relatively low temperature and high pressure [192].

The process depends on availability of waste heat in the power plant to provide thermal energy to the process in order to have a significant abate of CO_2. In the absence of these thermal sources, CO_2 abatement is almost null [186].

The methanol synthesis is composed by four main steps (Fig. 35):

1. H_2 production (water electrolysis unit)
2. Syngas compression
3. Methanol formation reaction
4. Methanol distillation

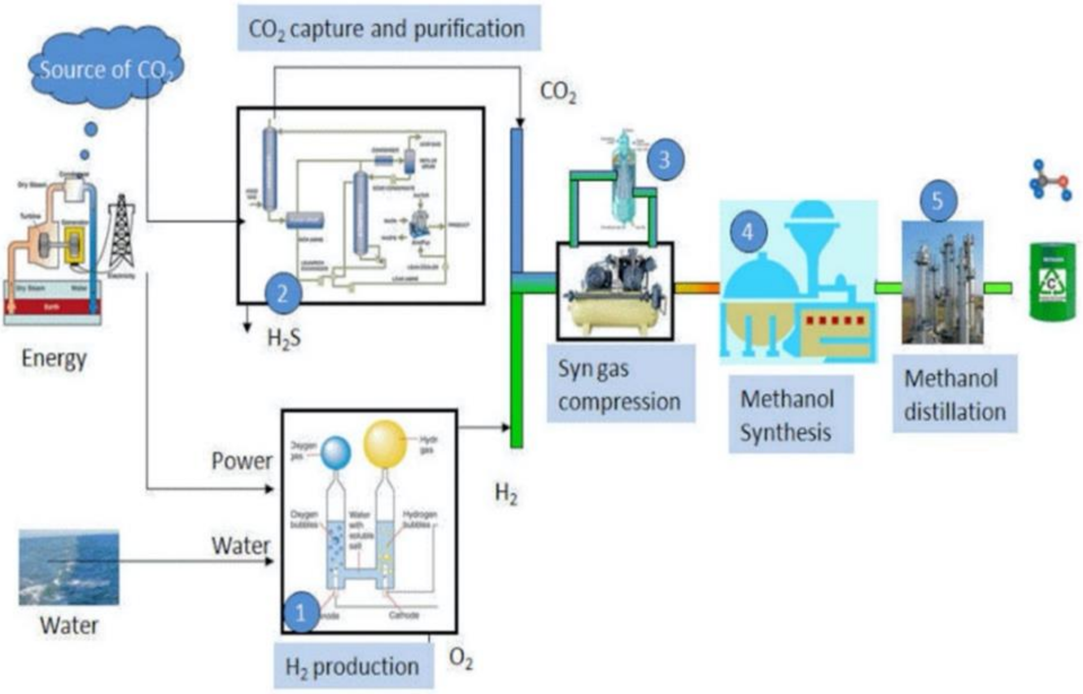


Fig. 35. Synthetic methanol production overview [193]

In methanol production (Fig. 35) the conversion rate is dependent on temperature, thus the key challenge in the design of reactor systems deals with the reaction heat rejection, to follow as close as possible the highest rate as the reaction advances. A significant number of concepts are commercially available today to achieve low catalyst volume, low outlet temperature (high conversion), heat recovery at high temperature (good energy efficiency) and low by-product formation. A possible concept consists in a multi-tubular reactor cooled with evaporating water, where each tube is filled with the solid catalyst.

Technology description

A model simulating both methane and methanol production plant is proposed. The first model aims to reproduce a system based on high-temperature steam electrolysis and methanation, while the second simulates a coupling between high temperature steam electrolysis and direct hydrogenation of CO_2 to produce liquid methanol. Both models were built using the software Aspen Plus^{TM}. For all simulations Peng-Robinson state equation has been chosen as thermodynamic model (Aspen Plus^{TM}, 2000). A scheme summarizing the main units and components for both the processes is presented in Fig. 36.

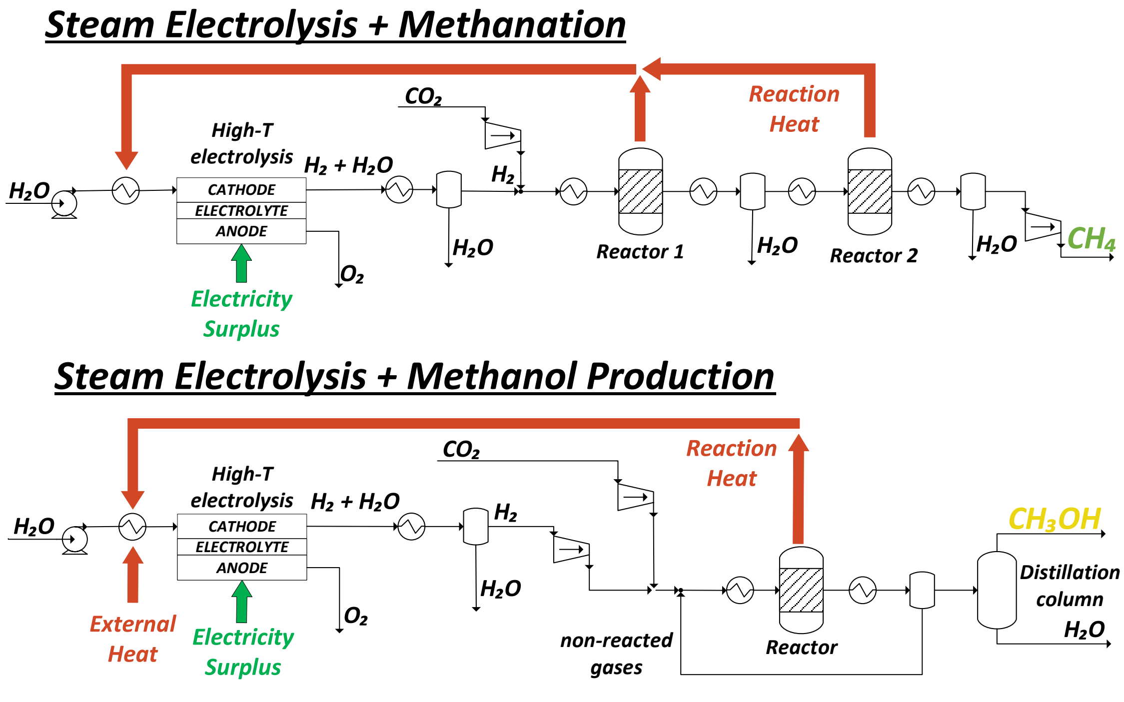


Fig. 36. A model simulating the proposed system operation for methane and methanol production plant

4.4.1. Electrolysis

The inlet water is pumped to compensate pressure drop during evaporation and to enable pressurized electrolysis at 15 bar, thus avoiding any further post-compression of the produced hydrogen at cathode side (in this process it has been assumed that methanation occurs at 15 bar). Reacting water is heated up to have superheated steam at electrolysis inlet. SOEC-based electrolysis unit has been modeled according to the water reduction reaction (6):

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{(Eq.6)}$$

A steam fractional conversion, also known as reactant utilization (RU), has been fixed to 80%. If the RU value is exponentially increased this may lead to an increase of diffusion overvoltage caused by the so-called starvation phenomenon. The cathode outlet is cooled down to 35 °C in order to condensate and remove water confined in the SOEC outlet stream, therefore shifting the chemical equilibrium of the subsequent catalytic hydrogenation reactions towards the products. In the Appendix an Aspen Plus^{TM} flowsheet demonstrates the electrolysis process modeling.

A plant size of 10 MW has been fixed to perform a system comparison between methanol and methane production: electrolysis power can be defined according to a First Law balance (Eq.7). The size has been iteratively calculated by adjusting the inlet water flow rate.

$$W_{el} = \sum n_{out} * \mathrm{h}_{out} - \sum n_{in} * \mathrm{h}_{in} = n_{out,cat} * \mathrm{h}_{out,cat} + n_{out,an} * \mathrm{h}_{out,an} - n_{in} * \mathrm{h}_{in} \qquad \text{(Eq.7)}$$

4.4.2. Fuel Synthesis

For both methane and methanol synthesis, inlet CO_2 is compressed up to the fixed hydrogenation pressure and then mixed with H_2.

Methanation unit consists of two isothermal intercooled reactors with intermediate condensation of the produced water, because H_2O removal shifts chemical equilibrium towards products (methane and steam). The reactors considered for the two-step methane synthesis are fixed bed isothermal reactors where boiling water on the shell side is used to remove the reaction heat (methanation is powerfully exothermal). Operating temperature (300°C) is controlled changing the pressure of the boiling water. The model used to describe this reactor is a PFR (plug flow reactor) under the following assumptions: one-dimensional heterogeneous model; negligible radial temperature gradient, and axial dispersion in the reactor tube; no temperature gradient through catalyst pellet. An inlet pressure of 15 bar has been set according to a previous work [184].

A Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model has been used as rate equation: kinetics for methane synthesis in a nickel-based catalyst has been taken from the open literature [194].

The transport phenomena as diffusion resistance within the catalyst pellet have been considered to evaluate the effect on reactor kinetics. The single spherical particle of catalyst can be treated as a porous medium. An equivalent diffusion coefficient (D_e) can be defined starting from the gas molecular diffusivity and other parameters related to the catalyst pellet as porosity and tortuosity: typical values can be found in the open literature [195].

The effect of transport limitation has been considered through the effectiveness factor, expressing the ratio between the moles of the reactant converted and the moles that would react if the concentration and the temperature inside were constant (Eq.8); where D_p is the diameter of the catalyst particle and k' is the ratio between the rate constant calculated with the LHHW expression and the concentration of the reactant in the catalyst volume. The effectiveness factors calculated (0.35÷0.4) are different for the two reactors because the CO_2 concentration is not the same.

Multiplying the kinetic factor of the LHHW expression by the effectiveness factor, it is possible to consider the effect of the CO_2 diffusion inside the pores of the catalyst (Eq.9).

$$\eta = 3/\varphi^2 * ((\varphi/\tanh\varphi) - 1) \qquad \text{(Eq.8)}$$

$$\eta = 3/\varphi^2 * (\varphi/\tanh\varphi) - 1) \qquad \text{(Eq.9)}$$

Where φ is the Thiele modulus

Methanol synthesis unit presents only one reactor with a recirculation of the non-reacted gases. The reacting stream is heated up to the reaction temperature and injected into the fixed bed isothermal reactor. After the reactor, water and methanol are condensed and separated from the non-reacted gases in a knock-out drum. Part of the non-reacted gases (5%) is purged to minimize the accumulation of by-products in the reaction loop. The liquid stream leaving the knock-out drum is called crude methanol: it is composed of methanol, water, and residual gases. The crude methanol is laminated to 1.2 bar through two valves before entering the distillation column.

The packed bed reactor is filled with $Cu/Z_nO/Al_2O_3$ commercial catalyst pellets. For this catalyst, the model proposed by Vanden Bussche and Froment can describe with good precision the reactions of methanol production and the RWGS reaction. The model assumes that the CO_2 is the main source of carbon for the synthesis. In addition, the model considers the inhibitory effect of water formed by the RWGS reaction. The activation energies of reactions were readjusted by Mignard and Pritchard to better represent the experimental data, which also expanded the application range of the model up to 75 bar [192] [196].

4.4.3. Upgrading

In the methane synthesis process a condenser enables the removal of nearly all the water produced during the hydrogenation reaction. A molecular sieve can retain residual water and carbon dioxide; the water in the gas pipeline should be maintain at low concentrations because the dew point of SNG must remain below a fixed value. The integration of two intercooled compressors brings the gas pressure to a value of 60 bar: a typical pressure value of natural gas in main pipelines.

In the methanol production plant, the residual gases contained in the flow that originates from the reactor, are completely separated from the liquid contained the reactor outlet (mainly composed by water and methanol) in a flash tank. The remaining stream is heated to 80°C in an exchanger and then directed to a distillation column. The column was simulated using the Aspen Plus^{TM} modelling tool known as ‘RadFrac’. The water is discharged from the bottom of the column at 102 °C; it contains a small amount of methanol and residual gases. Furthermore, gaseous methanol is discharged from the top section of the column at a pressure of 1 bar and temperature of 64°C; the discharge also contains small traces of water and non- reactant gases. During the chemical process, trivial amounts of by-products such as dimethyl ether (DME), alcohols, and other hydrocarbons may remain within the distillation column feed; hence leading to a possible accumulation of small amounts of methanol at the top of the column. However, this would not preclude its use as fuel [186]. Methanol is then compressed and cooled to 40°C and a flash drum separates non-reactant gases from liquid methanol.

Efficiency Analysis and Thermal Integration

Some parameters affecting energy analysis, such as the methanation reactors length, the CO_2/H_2 ratio and the methanol synthesis reactor temperature must be briefly discussed.

As a constraint for methanation unit, outlet CH_4 fraction has been set equal to 95 mol.-% (corresponding to a CO_2 conversion of $\approx$ 98.9 %). The length of the first reactor has been iteratively adjusted to minimize the overall length (i.e., the catalyst load) of the unit: the second reactor length follows because of the first reactor length, due to the constraint on the overall conversion. In other words, the second reactor must be long enough to enable the achievement of the specified conversion.

Such optimization led to fix the length of the first reactor equal to 1.2 meters (0.5 m for the second reactor), reaching an overall length minimum. This result has a fundamental importance in the following evaluation of the cost of the methanation system: the bare cost of the reactors and the cost of the catalyst inside the tubes of the reactors are minimized.

As seen in reactions (Eq.3), (Eq.4) and (Eq.5), three reactions occur in parallel in the methanol production: CH_3OH formation from CO and CO_2 and reverse water gas shift. Due to the equilibrium between the reactions and to the recirculation of the non-reacted gases, a sensitivity analysis to find the reaction temperature and the ratio between the reactants that allows the highest methanol production rate is required. During the design of the methanol production unit the electrolysis system size has been fixed to correctly compare the methane and methanol plant, implying a fixed hydrogen production. Temperature and H_2/CO_2 ratio affect the reaction kinetics. It is worth noticing that the methanol yield decreases when the CO_2 flow increases. Furthermore, by increasing the CO_2 feed some by-products are also produced (e.g., CO). Both CO_2/H_2 ratio and reaction temperature have been simultaneously adjusted in order to optimize the methanol synthesis unit: the maximum value for methanol yield was reached with values of 0.43 and 270 °C for CO_2/H_2 and temperature, respectively. During the optimization reactor length was kept constant.

Exothermal methanation reaction carried out within the catalytic reactors provides heat that could be used to evaporate the water required by the electrolysis section. Water pressure (affecting evaporation heat) can be iteratively adjusted to have a perfect match between heat generated (by the reaction) and heat required (by the evaporation). Pump outlet pressure results near 20 bar (against 15 bar needed within the electrolyzer), to make coincide the latent heat of evaporation of the water with the available heat at the two reactors. The following lamination in a valve allows to have the correct pressure at the SOEC inlet. For this reason, evaporation duty (as well as reaction heat) is not considered during the following thermal integration procedure.

Methanol synthesis reactor works in isothermal condition: reactor cooling is required to reject the reactions heat. The reactions that occur in methanol synthesis are less exothermic if compared to the CO_2 methanation: the heat available at the reactor is thus not enough to cover the thermal energy required by the evaporator as it occurred in the previous case. For this reason, the evaporating stream before the electrolyzer has been divided between the heat provided from the reactor and the heat that is needed from an external source.

Pinch analysis has been carried out to minimize the external heat requirement (i.e., maximizing efficiency) and to design the heat exchangers network (HEN). A minimum temperature difference between hot and cold streams has been set equal to 20 °C, in order to guarantee an optimum choice between the heat exchange area and the HEN cost [197].

Economic Methodology

The aim of this section is to illustrate assumptions and procedures in order to compare the methanol and methane production from an economic standpoint and understand how these technologies could fit in the current fuel market.

4.6.1. Cost Estimation Methodology

The capital expenditure calculation has been derived from the methodology proposed for the energy system studies by the National Energy Technology Laboratory (NETL) of the US Energy Department [12]. Four levels of capital cost have been considered: Bare Erected Cost (BEC), Engineering, Procurement and Construction Cost (EPCC), Total Plant Cost (TPC) and Total Overnight Capital (TOC). Furthermore, these four capital costs are labeled “overnight costs” and are expressed in “base-year” dollars. They do not consider financing costs nor escalation expenses. The base year is the first year of capital expenditure.

BEC is quantified based on an itemized list of all process equipment required for a project, together with the estimated cost of all materials and labor needed to complete the installation; furthermore, it is expressed in base-year.

EPCC encompasses the BEC plus the cost of services provided by the engineering, procurement and construction contractor, i.e., related to a contract arrangement used in some industries where the contractor is responsible for all services and activities related to the project. These services and activities include detailed engineering design, contractor permitting, and project/construction management costs. Usually, this additional cost varies between 8% to 10% of BEC: in this work a value of 9% has been assumed. TPC comprises the EPCC plus project and process contingencies.

Contingencies are funds added to the base cost estimate to compensate for cost estimate inaccuracies caused by uncertainty and risk exposure. For a small pilot plant, the project and process contingencies are estimated at 25% of BEC. This contingency is evaluated at 20% of the sum of EPCC and Process Contingency. TOC comprises the TPC plus additional overnight costs, including owner's costs. Owner's costs are composed of several addends: The Inventory Capital (calculated as 0.5% of TPC for spare parts); the land's cost (3000 $/acre plus a land surface of 2 acres were assumed); financing cost (estimated as 2.7% of TPC), the cost of securing financing the project, plus fees and closing costs; however, it does not include interest accrued during construction. Additional owner's costs were calculated as 15% of TPC [184].

If the TOC of a plant is known, it is possible to calculate the cost of the products through the net present value (NPV) analysis. NPV is the sum of all the discounted future cash flows and is determined by calculating the costs (negative cash flows) and benefits (positive cash flows) for each period of an investment; typically for one year. After the cash flow for each period is calculated, the present value of each one is achieved by discounting its future value at a periodic rate of return dictated by the market. Because of its simplicity, NPV is a useful tool to determine whether a project or investment will result in a net profit or a loss. A positive NPV results in profit, while a negative NPV results in a loss. The net present value can be calculated as (Eq.10):

$$\mathrm{NPV} = -\mathrm{TOC} + \sum_{\mathrm{n}=1}^{\mathrm{LT}} \frac{\mathrm{CFn}}{(1+\mathrm{i})^{\mathrm{n}}} \qquad \text{(Eq.10)}$$

The summation of all the cash flows (CF) considered in the analysis has been made up to the useful life of the plant, which in this work has been estimated at 30 years.

The cash flow has been calculated as the balance between the operating revenues, expenses and taxes (Eq.11):

$$\mathrm{CF_n} = \mathrm{Rev_n} - \mathrm{Exp_n} - \mathrm{Tx_n} \qquad \text{(Eq.11)}$$

The revenues are given by the sale of the desired product (methane or methanol) and by the oxygen by-product. Expenses are composed by the operation and maintenance (O&M) costs and by the costs of the external flows needed from the plants (i.e., electrical energy, carbon dioxide and water) (Eq.12).

$$Exp_n = FIXOM + UF * (VAROM + C_{CO2} * \ M_{CO2} + C_{el} + E_{el} + C_{H2O} * M_{H2O}) \qquad \text{(Eq.12)}$$

O&M are divided into two components; one that is depending on the operating hours of the plant, called variable O&M (VAROM), and the other that is constant called fixed O&M (FIXOM).

Yearly income taxes are calculated as the product between taxable income and tax rate. Taxable income is obtained by subtracting to operating revenues the operating expenses and the depreciation (Eq.13).

$$Tx_n = r_t * (Rev_n — Exp_n — Dep_n) \qquad \text{(Eq.13)}$$

The depreciation is a technical-accounting procedure for the distribution of a multi-year cost over the estimated years of life of the plant: it is constant and can be obtained dividing TOC over the amortization period, considered as the lifetime of the plant.

The final cost of the product (C_{prod}, expressed in \$/MWh) has been calculated as the selling price ensuring NPV equal to zero at the end of the operating life of the plant with a fixed discount rate (that is also an internal rate of return).

4.6.2. Calculation Assumptions

In this section the estimation of the BEC of the designed components (for both treated plants) was investigated. The equipment cost has been linked to an attribute of the component. The general formula (valid for various type of components) is the following (Eq.14):

$$\mathrm{Log}_{10} * C_p^0 = k_1 + k_2 * \log_{10}(A) + k_3 [\log_{10}(A)]^2 \qquad \text{(Eq.14)}$$

where A is the capacity or size parameter for the equipment and k_1, k_2 and k_3 are constant values depending on the specific equipment type. The previous formula provides the purchasing equipment cost for components operating at base conditions (C_p^0) which are identified by atmospheric operating pressure and a defined temperature level. In the open literature [198], the methodology to obtain the BEC for actual operating condition starting from base conditions is provided for some equipment. Operating conditions affect design and materials utilized. Pressure effect has been considered through a pressure factor (F_p) (Eq.15):

$$\log_{10} F_p = C_1 + C_2 * \log_{10}(P) + C_3 * [\log_{10}(P)]^2 \qquad \text{(Eq.15)}$$

where C_1, C_2 and C_3 are constant values depending on the equipment type and p is pressure expressed in bar(g). Temperature effect, and consequently the material choice, is represented by a material factor (F_M), that is provided by tables and diagrams. Therefore, the BEC can be calculated as (Eq.16):

$$C_{BM} = C_p^0 (B_1 + B_2 F_M * F_P) \qquad \text{(Eq.16)}$$

The values of B_1 and B_2 are given for different components. Both F_p and F_M are greater than one. For compressors and pumps the size parameters for the estimation of the purchasing equipment cost are the fluid power and the shaft power, respectively. Pressure factor F_p is present only for pumps, while material factors FM have been chosen considering the maximum temperature reached.

Cost estimation for heat exchangers is provided as a function of the heat exchange area. From the pinch analysis (which will be presented later) it is possible to calculate the surface for each exchanger (Eq.17):

$$\Phi = U \bullet A \bullet \Delta T_{ml} \qquad \text{(Eq.17)}$$

where Φ is the heat flow, U is the global heat transfer coefficient, A is the heat exchange area and ΔT_{ml} is the logarithmic mean temperature difference. U depends on the physical state (liquid, gaseous, phase changing) of the involved streams, temperature, and pressure. Heat transfer coefficient for each fluid coupling has been taken from literature [199]. Pressure factor F_p and material factor F_M have been used to calculate the purchasing cost of the equipment: for high-temperature heat exchangers a Ni-alloy was considered as material.

Fixed bed reactors have been designed considering the quantity, diameter, and length of the tubes. The considered reactors have the following shell-and-tubes structure: the reacting mixture flows inside the pipes that are filled with catalyst pellets; meanwhile outside each tube, the coolant (evaporating water) removes the generated heat. The bare cost of reactors has been estimated according to equation (Eq.14) and (Eq.15), considering them as shell and tube reactors and by utilizing the overall external tube area as cost parameter. The catalyst mass inside each reactor has been calculated; due to the catalyst deactivation it must be substituted to maintain the activity of the reactions at a chosen value. The cost and replacement expense of the catalyst will be discussed in a subsequent section. Comparable to the heat exchangers, pressure factor F_p and material factor F_M, have been used to calculate the purchasing cost of the equipment. The methanol reactor works at a high pressure (75.7 bar); hence, significantly affecting the cost.

Prices for the various components composing the distillation segment of a methanol plant can be obtained from the literature [200]. However, the available information is limited to specific component sizes; therefore, in order to scale and estimate the cost of a customized piece of equipment, the following relationship between BEC and size was utilized [198] (Eq.18):

$$C = C_0 \bullet (S/S_0)^f \qquad \text{(Eq.18)}$$

S is the equipment cost characteristic that can represent size or capacity and f is a cost scaling factor smaller than 1. Subscripts 0 refers to equipment with the base (i.e., available) attribute, and S depends on the considered component, in this case it corresponds to the flow rate. The scaling factor (sometime referred to a cost exponent) normally depends on the specific type of equipment. It is set to a default value of 0.6 giving the “six-tenths-rule” [87] when preferred estimation methods are not available.

The estimation cost of a SOEC, which is the component that has the greater impact on the plant cost, has been prepared by following information found in the literature [201]. The SOEC cost included in the economic analysis was realized by considering the perspective of market experts. The cost is contingent on several factors, such as the presence of research and development (R&D) financial backing that funding to support the innovations in materials and technology and the increasing in the production that strongly break down the prices (sometimes this is called RD&D that stands for Research, Development and Deployment). In this analysis four different cases were considered:

- The capital cost of a SOEC, considering current R&D financial funding and no production scale-up, is estimated to be 2500 €/kW by the year 2020 (this value represents the 10th percentile of the expert’s evaluations).
- The capital cost of a SOEC, considering current R&D financial funding and no production scale-up, is estimated to be 1050 €/kW by the year 2030 (this value represents the 50th percentile of the expert’s evaluations, i.e., the average value)
- The capital cost of a SOEC, considering current R&D financial funding and no production scale-up, is estimated to be 750 €/kW by the year 2030 (this value represents the 10th percentile of the expert’s evaluations).
- The capital cost of a SOEC, considering current R&D financial funding and production scale-up, is estimated to be 450 €/kW by year 2030 (this value represents the 10th percentile of the expert’s evaluations).

FIXOM

FIXOM is independent of the effective operating hours of the plant. The estimated costs of the plant include: the yearly catalyst replacement for methanation (valued at 15539 \$/m3) [12] and the catalyst replacement for the methanol reactor (fixed at 118 \$/kg) [200]. Other costs considered are the labor cost, set at 75,000 \$ per year/per worker. Considering that the plant is highly automated, only one operator is considered in the calculations [184]. The conventional maintenance cost has been considered equal to 0.5% of TOC. Also, the stack replacement of the electrolysis section must be considered. This replacement is associated with the cells limited life cycle. Usually, the lifetime of a stack is estimated at 5 years, but in this work the replacement cost is spread during the whole lifetime of the plant, considering it as the 2.5% of the TOC.

VAROM

VAROM depends on the Utilization Factor (UF), representing the ratio between the yearly operating hours of the plants and the total hours in a year. The costs usually considered are related to the external requirement of the system in terms of carbon dioxide, water, and electricity usage. In this work, the cost of CO_2 has been valued of 9 $/t. However, this CO_2 cost could oscillate between 3 $/t and 9 $/t over time [202]. Additionally, a long-term CO_2 avoidance cost is estimated at 0.43 $/t [181]. Other costs considered are water, set at 1 $/t [169]; electricity cost has been weighed at values ranging from 0 - 100 $/MWh to take into account various scenarios and the current electricity market price [200].

GLOBAL ASSUMPTION

Oxygen produced in the electrolysis section is a by-product that can be sold: its price has been considered equal to 79 $/t according to the open literature [203]. A tax rate of 20 % has been considered during the discounted cash flow analysis.

Energy prices in the EU depend on a range of diverse supply and demand market conditions that include geopolitical situation, the national energy mix, import diversification, network costs, environmental protection costs, severe weather conditions, and levels of excise and taxation. Natural Gas (methane) prices is affected by the end user; therefore, two different values (defining the price interval) have been considered: an industrial customer price equal to 37 $/MWh and a household customer price equal to 80 $/MWh. These values include taxes and levies for household consumers; however, it excludes refundable taxes and levies for industrial consumers (Eurostat, 2017, http://ec.europa.eu/eurostat.).

The methanol market involves a price volatility that is associated to the variation of crude oil prices. For this reason, an upper and a lower bound price have been considered ("Methanex Web page.," 2018, https://www.methanex.com). MeOH lower and upper bound prices have been set at 69 and 90 $/MWh (on LHV basis), respectively.

Results and Discussion

4.7.1. Thermal integration and plants energy performance

Figure 37 shows the composite curves for both the systems. Three zones should be noted: (i) the pinch point, i.e., where minimum temperature difference (20 °C) between hot and cold fluids occurs; (ii) the external heat requirement, represented by the difference between hot and cold composite curves in the right side of the charts; (iii) the wasted heat represented by the difference between hot and cold composite curves in the left side of the chart. In the methanation case, the plateaus corresponding to water evaporation (cold fluids) and reaction heat (hot fluids) are not presented. The reason being the good coupling between the available heat at the methanation reactors and the thermal requirement for the evaporation before the electrolysis.

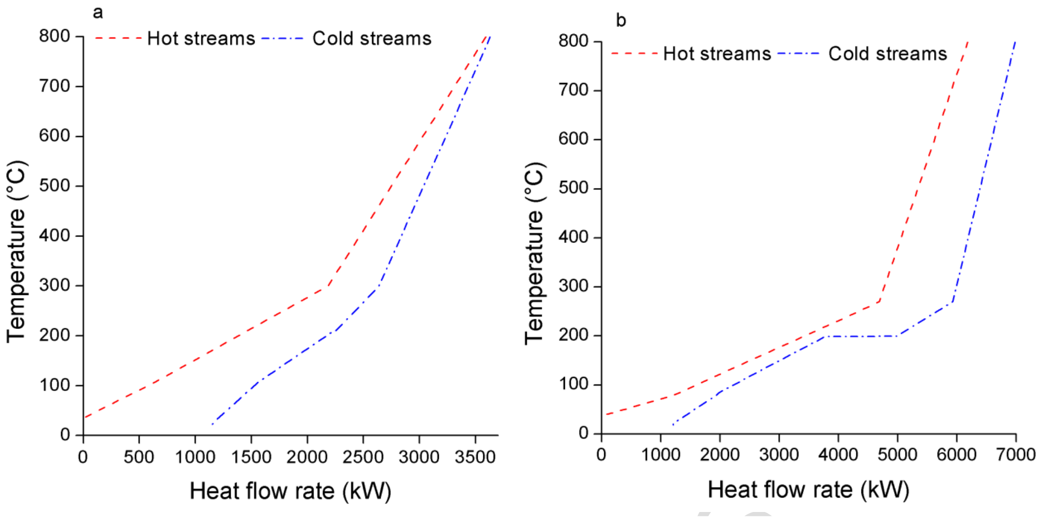


Fig. 37. Composite curves for hot and cold streams: methane (a) and methanol (b) synthesis

In Table 6 the main results related to the minimization of external heat are presented. The methanation plant demonstrates a superior integration because of its lower external heat requirement which eventually will affect the entire efficiency evaluation. The lower energy input for methane production is due to the ideal match between the heat produced (reaction cooling) and the heat required (evaporation). In the case of methanol, the rejected heat realized during the exothermal reaction can still be exploited to evaporate water; nonetheless it represents only a fraction of the required heat duty for evaporation. The heat produced by the reaction (145.2 kW) is smaller than the thermal energy required by the evaporator (436.6 kW). Only ≈ 33% of the evaporation heat is provided by the reactor cooling, while the remaining amount should be provided by external means or via thermal integration with hot process streams.

Table 6. Pinch Analysis Results for both plants

	SOEC + Methanation	**SOEC + Methanol production**
T_{pp} (°C)	790	209
$\Phi_{heat,min}$ (kW)	40	802
$\Phi_{cool,min}$ (kW)	1145	1210

The overall system efficiency can be calculated as the ratio between the chemical power of the products (methane and methanol) based on the heating value and the total energy input. This ratio is composed of the AC electric input for electrolysis, the power to drive compressors and pumps, and the energy required for the electric heaters needed to provide the external thermal energy.

Efficiency can be expressed through the following formula (Eq.19):

$$\eta = Power_{product} \div W_{el} = LHV_{product} * m_{product} \div W_{el} \qquad \text{(Eq.19)}$$

Table 7 summarizes the comparison between the two analyzed systems focusing on energy consumption, production, and performance. The higher compression work needed for the methanol production is due to the different pressure present in the methanation unit (about 15 bar) and in the methanol synthesis reactor (75 bar). Required electricity for pumping before electrolysis is slightly higher in the case of methanation, as the water pressure has been increased to allow the coupling of the heat requirement in evaporation with the thermal power available to the reactors of methanation, as previously pointed out. The total electricity requirement ($W_{el,input,TOT}$) takes also into account that electrolysis unit is fed with a direct current input: an AC/DC conversion efficiency of 98 % has been considered. It is worth noticing that the methanation process presents a higher efficiency if compared to the methanol production. This is mainly caused by two factors: the largest amount of external thermal energy needed by the methanol plant and the lower conversion rate in the methanol synthesis unit.

Table 7. Efficiency comparison between the analyzed plants

	SOEC + Methanation	**SOEC + Methanol Production**
$W_{in,SOEC}$ (kW)	10,000	10,000
W_{compr,CO_2} (kW)	118	319
$W_{compr,\ plant}$ (kW)	52	384
W_{pump} (kW)	5.9	4.4
$W_{external\ heating}$ (kW)	40	802
$W_{el\ input,\ TOT}$ (kW)	10,419	11,713
$LHV_{product}$ (MJ/kg)	50.2	19.9
Product mass flow (kg/s)	0.16	0.35
Chemical power (kW)	8,034	6,883
Energy requirement (kWh/kg)	18.1	9.4

4.7.2. Economic Results

Figure 38 shows the capital cost composition for methane and methanol plants. As presented, the SOEC cost impact is higher in the methanation plant because of the lower total investment cost with respect to the methanol plant. The higher pressure and the greater heat exchange duty needed in the methanol production represent the main cost difference between the two plants.

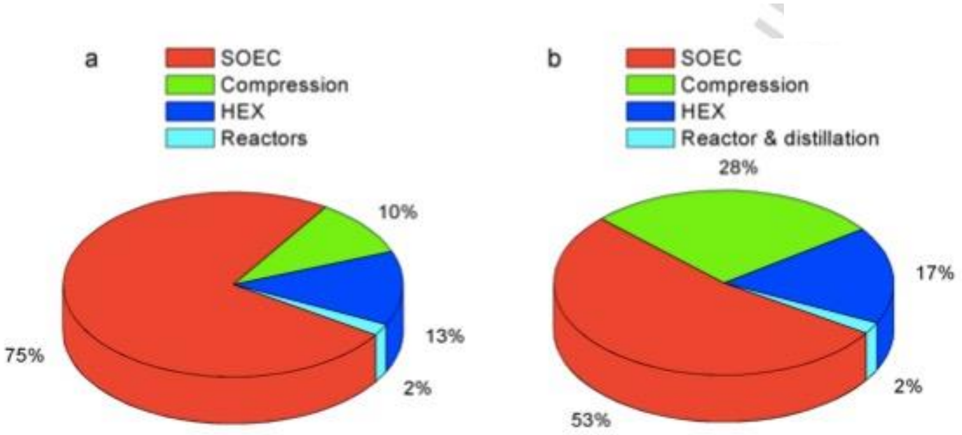
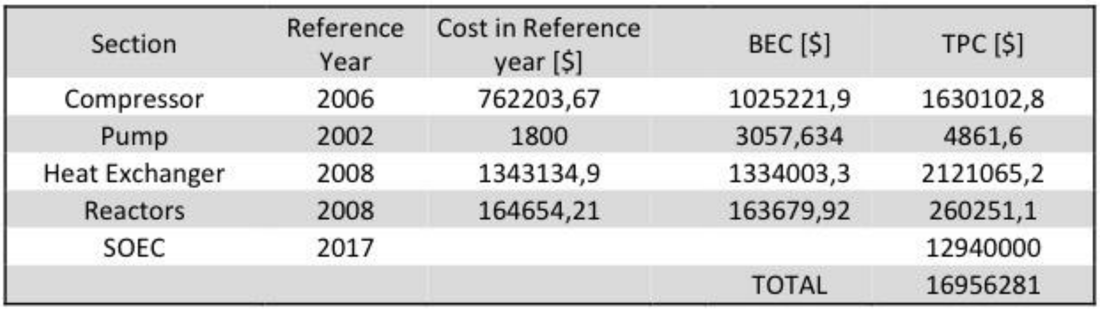


Fig. 38. Total plant cost sharing for the plants: methane (a) and methanol (b)

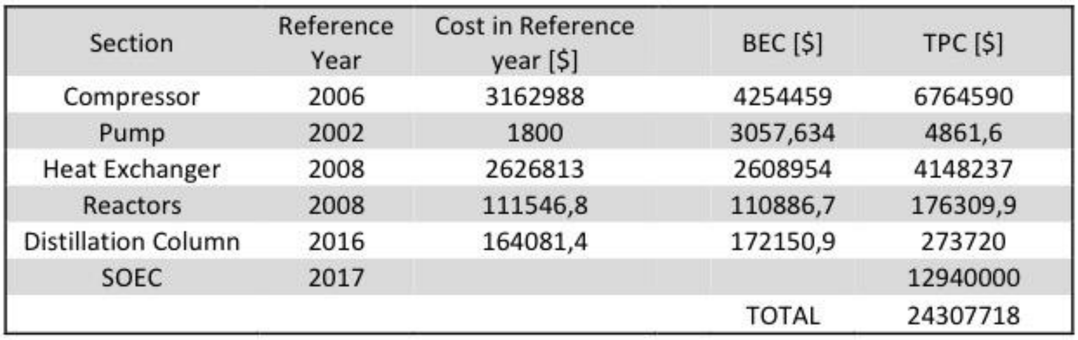
The total plant cost (TPC) for all the components of both plants needs to be escalated from the available year to the chosen base year. The base year to which all cost estimations refer to is 2017. The assumptions that are useful for capital cost estimation are summarized in the tables below (Table 8 and Table 9). The base cases for the economic analysis of both plants have been done considering a possible, near-term scenario in the SOEC price (2030 R&D 1 x 50th). Even though the TPC ($) for SOEC is the same for both plants, the pie charts above represent the share cost of all the components.

Table 8. Methanation Plant



Section	Reference Year	Cost in Reference year [$]	BEC [$]	TPC [$]
Compressor	2006	762203,67	1025221,9	1630102,8
Pump	2002	1800	3057,634	4861,6
Heat Exchanger	2008	1343134,9	1334003,3	2121065,2
Reactors	2008	164654,21	163679,92	260251,1
SOEC	2017			12940000
			TOTAL	16956281

Table 9. Methanol Production Plant



Section	Reference Year	Cost in Reference year [$]	BEC [$]	TPC [$]
Compressor	2006	3162988	4254459	6764590
Pump	2002	1800	3057,634	4861,6
Heat Exchanger	2008	2626813	2608954	4148237
Reactors	2008	111546,8	110886,7	176309,9
Distillation Column	2016	164081,4	172150,9	273720
SOEC	2017			12940000
			TOTAL	24307718

Table 10 summarizes the main economic results; these values are obtained considering the baseline assumption for some parameters such as: utilization factor (0.8), oxygen selling price (79 \$/t), and carbon dioxide cost (9 \$/t) (According to the IEA the price of CO_2 in 2017 for advanced economies ranges between 5-16 USD/tCO_2 and for emerging economies between 0-5 USD/tCO_2) [204]. Electricity cost in the base case has been set equal to 30 \$/MWh but it will be varied during the sensitivity analyses. The costs for a methanol synthesis plant are higher if compared to a methane plant. These expenditures are related to capital costs, O&M costs, and electricity (due to the lower power-to-fuel overall conversion efficiency). Moreover, the energy per year stored in chemical form is lower for the methanol plant. Although the two technologies are not so different in terms of economy return because of the competitive prices of the fossil methane in the actual market.

Table 10. Cost comparison between the plants

	CH_4 **synthesis**	**MeOH synthesis**
TPC ($)	16,956,281	24,307,718
TOC ($)	20,387,450	29,223,877
O&M ($/yr.)	687,789	858,379
CO_2 cost ($/yr.)	100,518	173,487
H_2**O cost ($/yr.)**	22,860	22,860
Electricity cost ($/yr.)	2,190,504	2,462,440
Energy production (MWh/yr.)	56,305	48,237

Figure 39 describes the variation of cost of the products as a function of the electricity cost, setting a utilization factor equal to 0.8, and by considering various scenario of the SOECs cost. 2,500 €/kW case illustrates the current SOEC price; the breakeven point is reached only if the electricity cost consumed is nearly zero (in the cases of "industrial natural gas" and "MeOH low price"). As shown in the scenarios on future cost reduction for SOECs, the breakeven point takes place at higher electricity price. The linear behavior of the lines describes the product cost, a linear dependence from the electricity cost. The slopes of these lines are steeper in the case of methanol; this means that the impact of the electricity cost is higher for the methanol due to the lower efficiency of methanol production. Each curve has been obtained with a carbon dioxide cost of 9 $/t.

When considering the household market prices of natural gas (NG) for a single-family household, it appears that the methanation process improves when compared to methanol production.

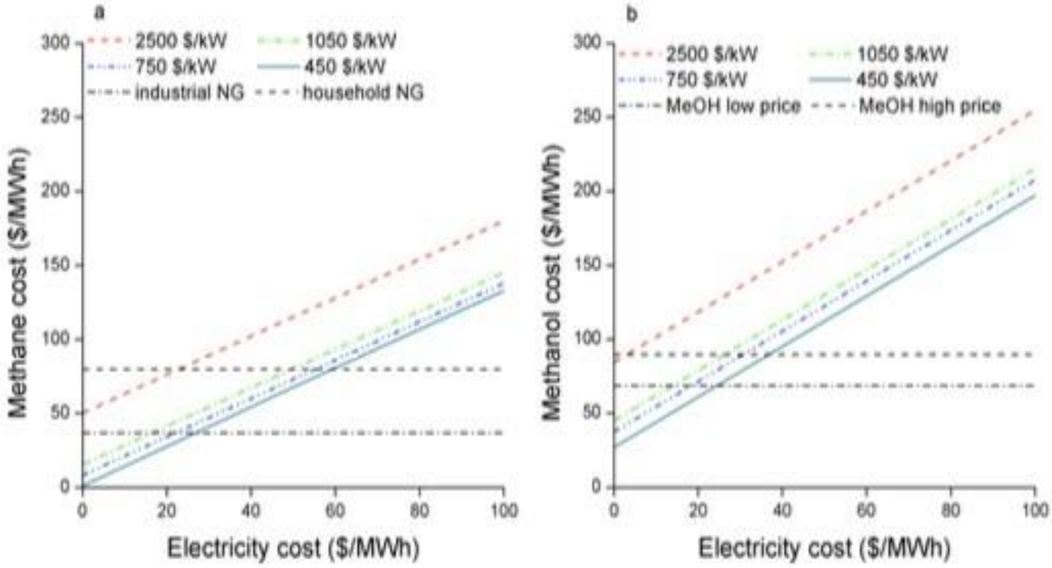


Fig. 39. Synthetic fuel cost by varying electricity cost and SOEC price scenario: methane (a) and methanol (b) synthesis

Figure 40 represents the cost of the products (methane and methanol, respectively) as a function of the electricity price, still setting a utilization factor equal to 0.8, for a specific SOEC cost equal to 1050 $/kW, but in this case the results are highly dependent on the cost of CO_2. The distance between the two lines is greater in the case of a methanol synthesis plant. The cause for this phenomenon is the higher amount of CO_2 required from the stoichiometry of the methanol formation reaction.

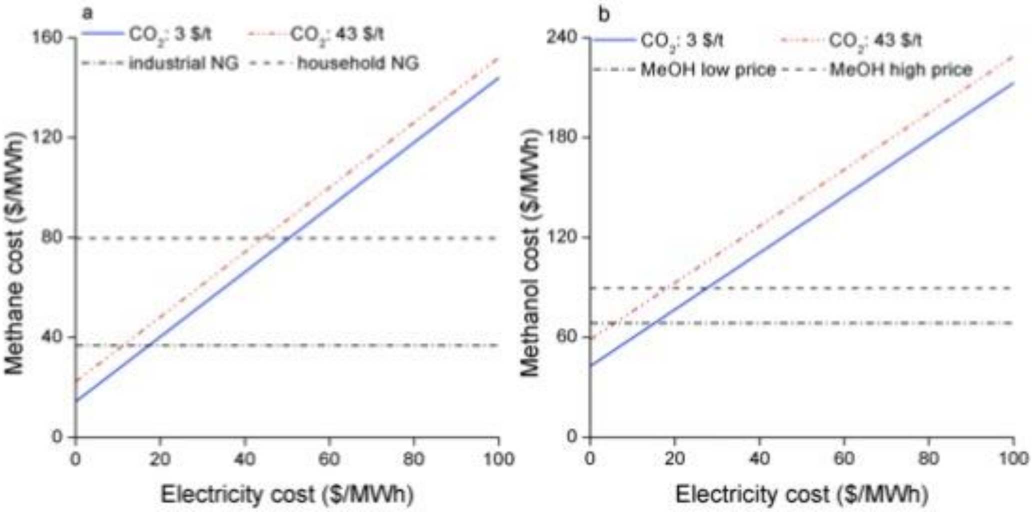


Fig. 40. Cost of the product vs. electricity price for different CO2 costs: methane (a) and methanol (b) synthesis.

Figure 41 shows the combined impact of the SOEC stacks specific cost and the utilization factor (UF) on the synthetic fuel price. In this last case some optimistic assumptions have been taken in order to simulate a future power-to-fuel scenario: the electrical energy cost has been set to zero considering that power-to-fuel plants should exploit surplus energy from a network that can provide the power free of charge, thus if the power-to-fuel system offer a service to the electric grid in terms of surpluses mitigation. In addition, the CO_2 cost has been fixed at 3 $/t, using the threshold value considered in the previous cases, awaiting those developments of carbon sequestration technologies become cost efficient, hence lowering the cost of captured CO_2. The tax rate has been set to zero, implying there is/are incentive/s provided by supportive entities interested in lowering the cost of these “green” technologies.

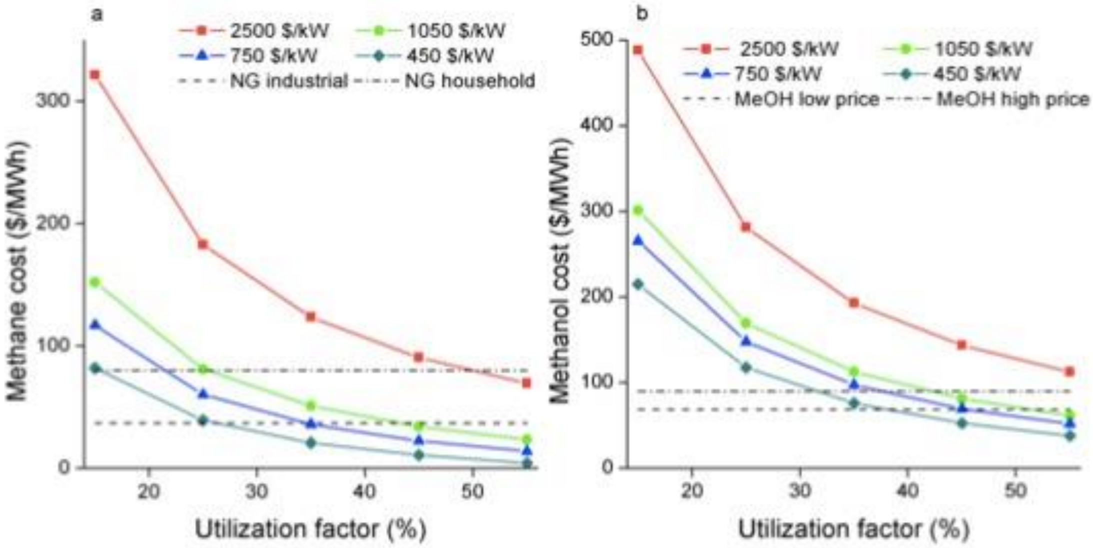


Fig. 41. Fuel cost by varying use factor and SOEC cost with electricity price = 0: methane and methanol

As expected, an increase of the utilization factor results in a lower synthetic fuel production cost. This is due to the lower impact of the capital expenditure; given this position remains equal while the number of equivalent operating hours (i.e., the produced fuel mass/energy) per year rises.

UF represents the fraction of the operating time during the year: in a power-to-fuel scenario the UF is not so high because it represents the time in which the electrical energy has a price close to zero. Considering the current price of a SOEC stack, the breakeven point is reached at UF equal to 50% for the NG household price, while a higher UF (≈ 85%, not shown in the figure) is required to compete with the current industrial NG market price. If the power-to-fuel system operates as an energy storage system; UF equal to 85% signifies frequent electricity surpluses (≈ 7500 hours per year). Nonetheless, when evaluating power-to-fuel operations in a more realistic manner, the value of UF becomes lower and the cost of electricity is cheap.

If a SOEC cost of 1050 €/kW is considered, the framework changes substantially; the breakeven point is attained with a UF equal to 45 % (that implies ≈ 4000 yearly operating hours) to reach a production cost comparable to the NG industrial price. As expected, as the breakeven UF decreases, the SOEC specific cost shrinks. Under the most optimistic assumption (i.e., free electricity, CO_2 price of 3 $/t and SOEC cost equal to 450 $/kW) the breakeven occurs at UF equal to 25 % (synthetic methane competitive with industrial fossil NG).

The situation is slightly different for methanol; with the current costs of SOEC, the creation of a competitive market can be achieved if UF is between 65% and 80% (not shown in the figure). In the scenario with SOEC cost equal to 750 €/kW, on the other hand, with a UF between 42% and 50% it is possible to compete with fossil-based methanol.

The very low cost of fossil NG for industrial use means that it is very difficult to contend the economic benefits if compared to synthetic natural gas. The production of methanol, on the other hand, compensates for the greater investment and operating costs with a higher market price. Results of this analysis show that the economic viability of power-to-gas for grid injection requires the reduction of capital cost (especially of the SOEC) and the availability of low electricity prices. Nevertheless, it is possible to generate revenue from financial investments if some major changes in the current development of the technology occur. Some of these changes are: boost R&D efforts (especially on electrolysis technology) and project costs optimization (e.g., mutualization of infrastructures, standardization of procedures and equipment). The exploitation of low-priced renewable electricity (e.g., 30 $/MWh for 6500 hours/year) requires an energy mix with very high share of technologically- mature wind and solar power produced by these sources and including their integration with other conventional power sources within the electric grid. This target could be achieved either through tax exemptions, policy incentives or specific project configurations (e.g., power-to-gas plant located close to industrial sites already exempted from the tax or to baseload production plant, depending on the regulation framework), amongst other possible solutions.

Finally, with a review of the economic analysis for the methanol plant it was evident that the commercialization of a cost-efficient technology could be achieved in the medium to long term (approximately 15-20 years) (Dairanieh et al., 2016). It is imperative that resources are invested in R&D efforts, especially those related to electrolysis technology and scale effects of the SOEC system. Moreover, the power-to-methanol process could become economically viable if the fuels produced by the plant are not taxed (i.e., competing with prices of taxed-gasoline).

Mineral Carbonation of Fly Ash

Coal fired thermal power plants are large emitters of CO_2; however, coal is extensively relied upon for power generation. Furthermore, coal combustion also produces ashes (e.g., fly ashes), a solid byproduct, usually discarded in landfills or waterways. To be able to continue the use of coal for energy production, low-cost technologies must be developed for capturing, utilizing, and storing CO_2 (CCUS). One possible CCUS solution entails the practice of using hi-tech applications for capturing CO_2 from the flue gas of a coal power plant; the recovery of fly ashes produced by the combustion of coal; the mineral carbonation (MC) process to produce carbonated fly ashes (CFA); and the use of these ashes for the concrete/construction industry.

Mineral carbonation is a CCUS technology that can capture large amounts of CO_2 and convert it to solid inorganic carbonates using chemical reactions. MC is one of the only options that results in permanent storage of CO_2 as a solid, with no need for long term monitoring. Due to the product's stability over long periods of time it makes it ideal for the construction industry; furthermore, it eliminates the concern of potential CO_2 leaks that could pose safety or environmental risks.

Current R&D activities in MC are focused on attaining energy efficient reactions and reaction rates feasible for storage of substantial volumes of CO_2 from industrial processes by means of industrial waste such as fly ash. (accelerated mineral carbonation).

Fly ash, an inorganic deposit remaining after coal combustion, is divided into two groups: Type F (low-calcium) and Type C (high-calcium) a.k.a. high-calcium fly ash (HCFA) [205]. The two types of fly ash are based on its source of origin and composition (i.e., type of coal that is burned). Type F fly ash is normally produced from burning anthracite or bituminous coal whereas HCFA is produced from burning lignite or sub- bituminous coal. HCFA, for the most part, is preferred over Type F fly ash because of its higher content of calcium. When HCFA is used as a complementary cementitious material it can augment some of the physical, behavioral, and structural properties of the concrete (e.g., compressive strength, workability, etc.). Nevertheless, when "carbonated" HCFA is used as a complementary cementitious material it can boost some of these concrete properties if compared to the use of just HCFA [206].

The prospective for using fly ash as a complementary cementitious material in concrete has been known almost since the start of the last century, although it wasn't until the mid-1900s that significant utilization of fly ash in concrete began following the pioneering research conducted at the

University of California, Berkeley [207]. The last 50 years has seen the use of fly ash in concrete grow dramatically with close to 15 million tons used in concrete, concrete products and grouts in the U.S. in 2005 [208].

The use of fly ash has great prospective to diminishing GHG emissions by reducing mining activities, decreasing CO_2 production during the production of materials that can be substituted by fly ash (e.g., Portland cement), minimizing the disposal problem usually in storage ponds, and helping in the improvement of land utilization. However, the prospective of a new route of cementation by the carbonation of fly ash is still under development but with great potential for accelerated commercialization. The escalation of environmental and economic benefits created by this new pathway for cementation are significant if compared to the current methods of using fly ash in the construction industry.

The work utilizes the data of a recent experimental investigation preformed at UPC as part of a work's analysis. The experiment consisted of the accelerated carbonation of HCFA under dry and moist conditions, at various temperatures and pressures. The HCFA (consisting of 35.27% CaO) used in the UPC experiment came from a coal plant located in Greece. The source of the CO_2 utilized in the experiment was intentionally mixed in the lab with the purpose of mimicking "untreated" CO_2 (i.e., the unadulterated flue gas from a coal power plant= 84% NO_2, 14% CO_2, 1% H_2O). The experiment demonstrated that the highest carbonation efficiency (55.2% and 132.7 g/CO_2/kg fly ash, related to the total CaO %) came from HCFA in dry conditions, at 160°C, 2 hours, and 6 bars. However, results showed that rising the pressure and temperature enhances the process of carbonation, as well as the presence of moderate amounts of water vapor in the CO_2 gas flow [205]. The study ultimately concluded that approximately 21% of all CO_2 emissions of a coal-burning power plant could potentially be sequestered as carbonates (Fig. 42) [206].

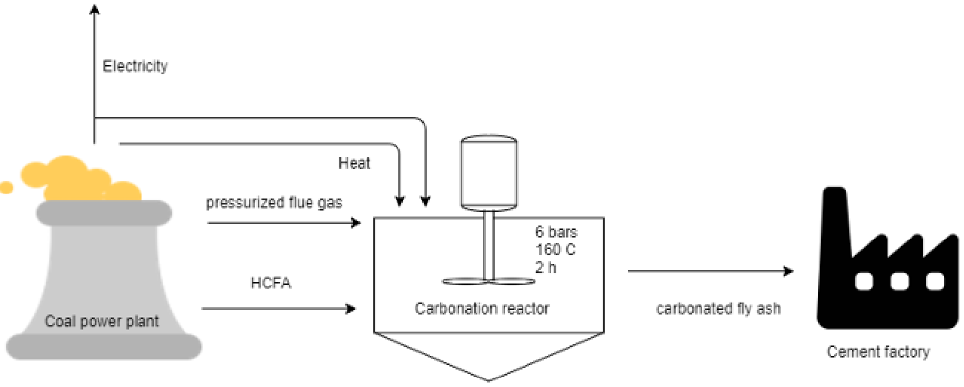


Fig. 42. Simplified schematic of UPC's experimental HCFA carbonation process

Highlights of the HCFA carbonation process:

- Carbonation reactor has a small footprint and is placed near the coal power plant

- Flue gas from the coal gasification is already pressurized (6 bars) and is redirected to the carbonation reactor
- HCFA with 21% content of free CaO is transferred to the carbonation reactor immediately after production from coal processing (2 tons of fly ash is carbonated over 2 hours)
- Carbonation reaction conditions: 6 bars, 160 C^0, 2 hours for 1 part of fly ash fitting to the reactor size (2 tons). The reaction inside the reactor is:

$$CaO + CO_2 \rightarrow CaCO_3 \; (\Delta H = -167 \, \frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}})$$

Carbonation of HCFA ashes has two benefits: (i) reduction of CO_2 emissions produced by fossil fuel power plants and (ii) increase the utilization rate of these fly ashes [209] [210] [211]. Carbonation process changes properties of HCFA by lowering the free lime content, what in consequence can allow the use of this material for cement production [212] [213] [214].

This Chapter also identifies parallels and nonconformities between fly ash (mainly HCFA) classifications ASTM International and EU Standards of the most frequently used specifications governing certain cement and concrete applications. Technological advances in fly ash applications are developing rapidly; however, the shortage of regulatory reaction to these technological advances may impede the adoption of those technologies

Finally, the Chapter assesses the market and business potentials for developing new fly ash configurations (e.g., carbonated fly ash) and its use in the construction industry.

Mineral Carbonation

Under the framework of CCUS, there is a process called accelerated carbonation (chemical adsorption). In this process, alkaline materials are reacted with CO_2 in the presence of moisture to accelerate the reaction to a timescale of a few minutes or hours [215]. CO_2 utilization by mineralization as carbonates is related to the accelerated carbonation technology (ACT). Mineral carbonation is one of few technologies that work as both capture and storage technologies [216]. One of the advantages of MC is the stability of the formed carbonated products over extended periods of time. Thus, there would be little need to monitor the disposal sites and the associated risks would be very low [217].

The basic goal of accelerated carbonation is to mimic the natural silicate rock weathering processes in which CO_2 reacts with metal oxide bearing materials to form stable and insoluble carbonates, with calcium- or magnesium-oxide being the most favorable metal oxide in reacting with CO_2 (Fig. 43). The process is exothermic and thermodynamically favored, with typical enthalpies of reaction ranging from 50 to 100 kJ/mole, depending on the resource materials utilized [218] [219].

The energy demand for mineralization is high mainly to overcome the slow reaction kinetics, as high reaction pressures and temperatures are recommended [220]. Factors that affect the kinetics of the carbonation reaction are exposure conditions, such as CO_2 partial pressure, source and concentration, temperature, water/vapor content, porosity and permeability [221].

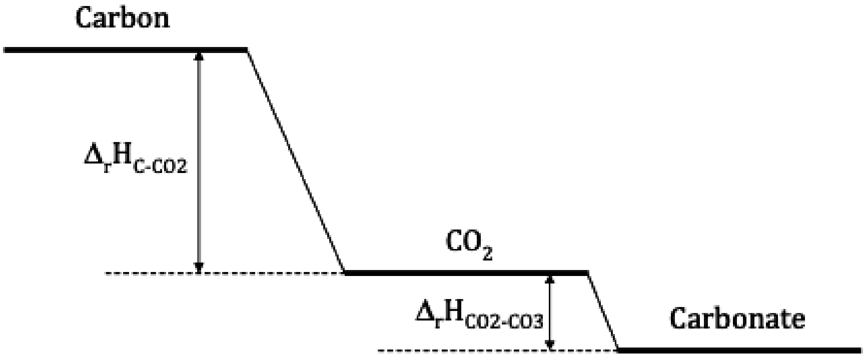


Fig. 43. Thermodynamic stability diagram of carbon [220]

Industrial residues such as steel making slags, combustion residues, waste concrete, fly ashes, etc. are alkaline and also appear to be potential raw materials for CO_2 sequestration by accelerated carbonation because these materials are generally rich in metal oxides including calcium, magnesium, aluminum, iron, and manganese oxide [222].

Currently, accelerated carbonation processes have been focused on assessing and maximizing the storage of CO_2 by optimizing the operating conditions including pressure, retention time, temperature, gas-to-solid (G/S) ratio in direct routes, gas-to-liquid (G/L) ratio and gas-liquid-solid (G/L/S) ratio in aqueous routes, gas humidity, gas flow rate, liquid flow rate, particle size, and solid pretreatment processes [223].

Mineral carbonation encompasses a series of reactions that can take place in a single or a multi-step process, also known as direct and indirect carbonation, respectively [224]. In a single-step process, the extraction of the metal from the mineral medium and the carbonate precipitation occurs simultaneously in the same reactor [225]. Direct carbonation takes place under high pressure conditions in either dry or aqueous media. Multi-step or indirect carbonation is when alkaline earth metal is first extracted from the mineral matrix and subsequently carbonated, it usually involves pre-treatment of used minerals Fig. 44. [223].

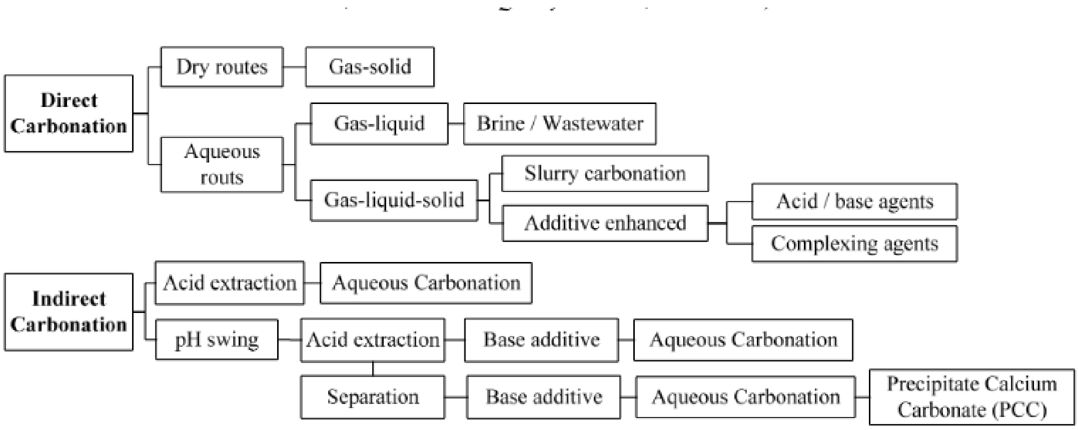


Fig. 44. Various process routes of accelerated carbonation for CO2 capture [225]

The process of MC of CO_2 offers a pathway for long-term storage as part of the CCUS procedure. CO_2 reacts with Ca or Mg-rich minerals to form a carbonate along with the release of heat energy, as shown in Equation (1) to Equation (4), [226]. The strategy consists in activating abundant natural silicate rocks, such as wollastonite ($CaSiO_3$), olivine (Mg_2SiO_4), and serpentine ($Mg_3SiO_5(OH)_4$) [227] [228]:

$$\mathrm{CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2}\ \left(\Delta H^\circ = -90\,\frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}}\ \text{wollostonite}\right) \quad \text{(Eq.1)}$$

$$\mathrm{Mg_2SiO_4 + CO_2 \leftrightarrow 2MgCO_3 + SiO_2}\ \left(\Delta H^\circ = -89\,\frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}}\ \text{olivine}\right) \quad \text{(Eq. 2)}$$

$$\mathrm{Mg_3SiO_5(OH_4) + 3CO_2 \leftrightarrow 3MgCO_3 + 2SiO_2\ +\ 2H_2O}\ \left(\Delta H^\circ = -64\,\frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}}\ \text{serpentine}\right) \quad \text{(Eq.3)}$$

$$\mathrm{CaO + CO_2 \leftrightarrow 2CO +\ 2H_2}\ (\Delta H^\circ = +247\,\frac{\mathrm{kJ}}{\mathrm{mol_{CO_2}}}) \quad \text{(Eq. 4)}$$

The use of pure CO_2 is not vital for mineral carbonation as the presence of impurities such as NO_x in flue gas will not restrict with the carbonation reaction [57]. Therefore, the separation and capture step that produces a pure stream of CO_2 can be omitted as waste emissions containing CO_2 can be used directly [125].

The main advantage of MC is the formation of stable carbonates capable of storing CO_2 for long periods of time [229], without the risk of CO_2 leakage as in CCS [230]. However, this technology is not fully matured for large-scale applications as the energy penalization and costs are still too high [231].

In the case of silicate rocks, carbonation can be carried out either ex-situ in a chemical processing plant after mining and pretreating the silicates, or in-situ, by injecting CO_2 in silicate-rich geological formations or in alkaline aquifers [232]. In-situ carbonation is an operation similar to geological storage, while ex-situ carbonation involves processing steps requiring additional energy input that are difficult to compensate for with the energy released by the carbonation reaction [233]. Following the lab experiments conducted at UPC this chapter will focus on processes and practices that follow ex-situ mineral carbonation and direct carbonation routes [234].

Mineral carbonation offers the opportunity to create products and generate applications that implements CCUS processes. Direct and indirect carbon mineralization of natural and industrial alkaline materials offer the opportunity to produce a range of tailored carbonation products and by-products as construction and building materials [235] [236]. Process adaptation or post-processing can be employed to further expand the range of products to include higher-value ones. Applications include structural materials (e.g., cements, concrete, and mortars), nonstructural materials (e.g., for road-base, erosion, sea, and flood protection barriers), and calcium- and magnesium-based carbonates that may be used for different applications (e.g., as additives for protective coatings such as paints and polymers) [237]. In construction applications carbonate solids can provide cementitious binding of the components of the building product, or structural support (as an aggregate or filler) [238]. Furthermore, the carbonation of alkaline industrial waste may also be applied to immobilize or extract heavy metals, stabilize chemically metastable mineral phases, or even store energy or provide carbon to microalgae [239].

Furthermore, waste materials such as steel slag, bauxite residue and air pollution control (APC) residues are good candidates for conversion into building materials using CO_2. Companies in different parts of the world are scaling up businesses using these waste materials; together they consume around 75 kilo tonnes (kt) of CO_2 annually. The British company Carbon8 uses around 5 kt/yr. of CO_2 to convert around 60 kt/yr. of APC residues into lightweight aggregates as a component of building materials [240].

Fly Ash

Fly ash is a by-product of coal combustion power plants [241]. Compared with natural minerals, it has numerous advantages as a feedstock for carbon dioxide mineral carbonation, including low materials cost, high reactivity, absence of pretreatment requirement, and ease of availability near CO_2 emission sources [84]. Specifically, fly ash usually has alkaline oxides such as calcium oxide (CaO) and magnesium (MgO), which are the perfect feedstocks for CO_2 sequestration because of their high reactivity [242].

According to ACI 116R, fly ash is a pozzolanic material that is defined as siliceous or siliceous and aluminous material and possesses little or no cementitious value [243]. When it reacts with calcium hydroxide (lime) in the presence of water it forms a soluble compound that encompasses cementitious properties similar to cement. Pozzolanic activity of fly ash is an indication of the lime fly ash reaction. It is mostly related to the reaction between reactive silica of the fly ash and calcium hydroxide which produce calcium silicate hydrate (C-S-H) gel which has binding properties [244].

The main objective of using fly ash in most of the cement concrete applications is to get durable concrete at reduced cost. Concrete is a heterogeneous mixture of cement, aggregate, and water which when mixed thoroughly form a rock like structure capable of withstanding heavy loads [229]. When cement gets reacted with water it tends to form a cementitious gel which is capable of binding different materials together.

This process of reaction between cement and water is named as hydration[1] [245] and it is an exothermic process i.e., heat gets evolved during this process, at the same time some quantity of calcium hydroxide is also formed which doesn’t have any impact on the strength point of view on concrete in that state (Fig. 45) [246].

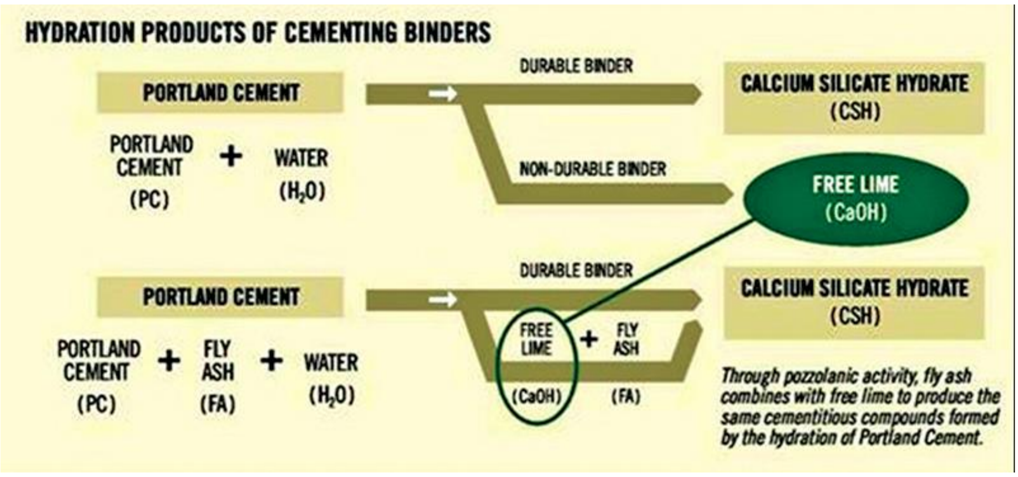


Fig. 45. The process of hydration [214]

The process of hydration:

Portland cement + H_2O = (C-S-H) + Ca (OH) 2{free lime liberated}
Fly ash + Ca (OH) 2 = (C-S-H) {additional cementitious paste}
(C-S-H) -Calcium Silicate Hydrate

The process of hydration accounts for the use of Portland cement. Portland cement (or Ordinary Portland cement- OPC) is the most common and inexpensive type of cement in general use around the world as a basic ingredient of concrete, mortar, stucco, and non-specialty grout [206]. According to ASTM C150, Portland cement is a hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers which

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[1] The cement in concrete mix liberates free lime when it starts to hydrate with water. Fly ash in concrete mix produces cementitious paste by reacting with this free lime only. Fly ash in concrete mix can be active only after the availability of sufficient free lime, hence fly ash component of concrete starts reacting after a little while only.

consist essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter-ground addition [247].

It is well known that the production of cement is a major source of greenhouse gas emissions, accounting for about 8 percent of all such releases [218]. The production of cement releases greenhouse gas emissions both directly and indirectly: the heating of limestone releases CO_2 directly, while the burning of fossil fuels to heat the kiln indirectly results in CO_2 emissions [222].

The direct emissions of cement occur through a chemical process called calcination. Calcination occurs when limestone, which is made of calcium carbonate, is heated, breaking down into calcium oxide and CO_2. This process accounts for ~50 percent of all emissions from cement production [230].

Indirect emissions are produced by burning fossil fuels to heat the kiln. Kilns are usually heated by coal, natural gas, or oil, and the combustion of these fuels produces additional CO_2 emissions, just as they would in producing electricity [248]. This represents around 40 percent of cement emissions. Finally, the electricity used to power additional plant machinery, and the final transportation of cement, represents another source of indirect emissions and account for 5-10 percent of the industry’s emissions (Fig. 46) [222].

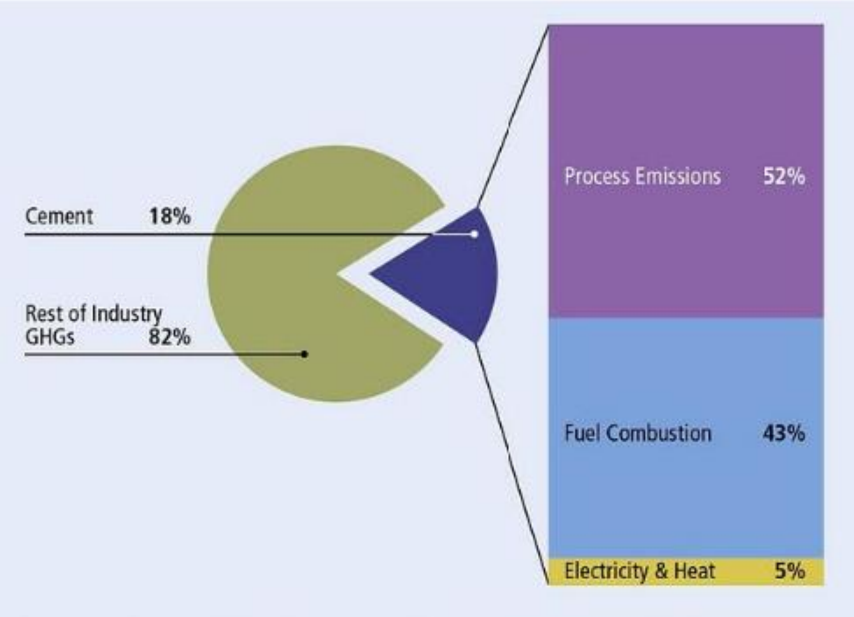

Fig. 46. CO_2 emissions from cement manufacture [224]

The use of fly ash as partial replacement of clinker in cement or as direct addition to the concrete solves an environment problem for the setting and the power plant [249]. The fly ash as a substitute of the cement will also provide a profit by reducing CO_2 emission in the cement production process, and an energy saving when fly ash replaces some of the energy- intensive produced cement [250]. Production of 1 ton cement generally produces 1 ton CO_2 [207].

Another benefit is the reduction of toxic metals and radon in fly ash deposed into ponds and landfills [251]. Fly ashes may contain very small amounts of toxic metals that are leachable [252]. Incorporation of fly ash in concrete solves this problem because hydration products of both Portland cement and blended Portland cement can form complexes that permanently tie up the toxic cations released by fly ash [3].

Historically, fly ash has been used in concrete at levels ranging from 15% to 25% by mass of the cementitious material component.; these levels can improve some of the durability and structural properties of concrete, especially long-term compressive strength and heat of hydration [253] [254]. The actual amount used varies widely depending on the application, the properties of the fly ash, specification limits, and the geographic location and climate. Higher levels (30% to 50%) have been used in massive structures (for example, foundations and dams) to control temperature rise. In recent decades, research has demonstrated that high dosage levels (40% to 60%) can be used in structural applications, producing concrete with good mechanical properties and durability [255].

According to ASTM C618, the most widely used specification of fly ash in North America, divides fly ash into two classes based on its source of origin and composition. The two classes are: Type F (low-calcium ≤ 8% CaO) and Type C (high-calcium ≥ 20% CaO) a.k.a. high-calcium fly ash (HCFA) [256]. The two types of fly ash are based on its source of origin and composition (i.e., type of coal that is burned). However, the variation of the fly ashes is not only attributed to the source of origin, but it can also vary within the same plant [257].

Nonetheless, the European specification BS EN 197-1 has another definition for Type F and Type C fly ashes called Type V and Type W respectively. The main difference between these classes is the amount of calcium, silica, alumina and iron. Tables 11 and 12 summarizes the differences.

Table 11. Some definition of fly ash types according to EN 197-1 and ASTM C618 [258] [259]

	Low calcium fly ash	**High calcium fly ash**
Fly ash from	Bituminous coal and anthracite	Subbituminous and lignite
Reaction characteristic	Pozzolanic	Pozzolanic and hydraulic
Definition by EN 197-1	**Type V: Siliceous fly ash**	**Type W: Calcareous fly ash**
	≤ 10% reactive CaO ≥ 25% reactive SiO2 < 5% LOI < 1% free lime	≥ 10% reactive CaO ≥ 25% reactive SiO_2 when CaO is 10-15% If CaO > 15% the compressive strength ≥ 10 MPa at 28 days (NS-EN 196-1) < 5% LOI
	Class F	**Class C**
Definition by ASTM C618	$SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$ Free moisture, max. 3.0% LOI, max 6.0% SO3, max 5.0% CaO, max: no limit Amount retained when wet sieved on 45 µm: Max. 34%	$SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50\%$ Free moisture, max. 3.0% LOI, max 6.0% SO3, max 5.0% CaO, max: no limit (Note: CaO > 10%) Amount retained when wet sieved on 45 µm: Max. 34%

Table 12. Typical values for fly ash Type F and Type C [260]

	Typical values (wt.%)	Class F	Class C
SiO_2	35-60		
CaO	1-35	< 15wt.-%	>15 wt.-% (in Canada Class CI: 8-12% Class C> 20%
Fe_2O_3	4-20		
Al_2O_3	10-30		

Fly ashes consist mostly of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) [261]. The pozzolanic properties of the fly ash are not governed so much by the chemistry but by the mineralogy and particle size of the ash [262]. Variations in the chemical composition of fly ashes are, therefore, natural. These governing properties of the ashes are credited to the coal-fired furnace which are controlled by the type of coal and the processing conditions of the furnace [257].

There are basically four types of coal, each vary in heating value, chemical composition, ash content, and geological origin [263]. Type F fly ash is normally produced from burning anthracite[2] or bituminous[3] coal whereas HCFA is produced from burning lignite[4] or sub- bituminous[5] coal [264]. Table 13 shows the chemical compositional of the three most common types of coal [264]. HCFA, for the most part, is preferred over Type F fly ash because of its higher content of calcium [244]. However, utilization of HCFA is limited in order to avoid delayed carbonation of excess lime and the subsequent appearance of microcracks due to the expansive nature of such carbonation reaction. This limitation leads to most of HCFA materials being currently collected in storage ponds [10]. With the present practice of HCFA disposal in ponds (generally in the form of slurry), the total land

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[2] Anthracite is the highest rank of coal. It is a hard, brittle, and black lustrous coal, often referred to as hard coal, containing a high percentage of fixed carbon (86-97%) and a low percentage of impurities. processes a higher amount of heat per unit mass than the other types of coal. It does not ignite easily and does not produce smoke; therefore, it burns cleanly.

[3] Bituminous coal is a middle rank coal between subbituminous and anthracite. Bituminous coal is the most abundant type of coal. It is often called soft coal and it has slightly lower carbon content than anthracite (45-86%) and there is water, hydrogen, sulfur and few other impurities. It is soft and contains a substance called bitumen, which is like tar. Bituminous coal is produced from sub bituminous coal when it undergoes more organic metamorphism.

[4] Lignite is used almost exclusively for electric power generation lignite is a young type of coal. Lignite is brownish black, has a high moisture content (up to 45 %), and a high Sulphur content. Lignite is more like soil than a rock and tends to disintegrate when exposed to the weather. Lignite is also called brown coal.

[5] It does not have the same shiny luster as higher ranked coals. As the name suggests, it has lower carbon content than bituminous coal (35%-45%) and is primarily used for electricity generation

required for ash disposal is approximately 82,200 ha [243]. Consequently, disposal and management of HCFA is a major problem in coal-fired power plants.

Table 13. Chemical composition for fly ashes produced by different coal types [264]

Components (wt.%)	Bituminous	Sub-bituminous	Lignite
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	10-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
Mg	0-15	1-6	3-10
SO_3	0-4	0-2	0-10
Na_2O	0-4	0-2	0-6
K_2O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

Type F: produced by the burning of harder, older anthracite and bituminous coal with more than 70wt% of $SiO_2 + Al_2O_3 + Fe_2O_3$. This fly ash is pozzolanic in nature and displays no significant hydraulic behavior. Possessing pozzolanic properties, the glassy silica and alumina of Type F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds [265].

Type C (HCFA): High Calcium Fly Ash, is rich in calcium oxide (10-50%), produced from the burning of younger lignite or sub-bituminous coal, with contents of $SiO_2 + Al_2O_3 + Fe_2O_3$ between 50 and 70%, with varying amounts of carbon as measured by the loss of ignition (LOI) [249]. Lignite and sub-bituminous coal fly ash is characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as lower carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash [264].

In addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Type C fly ash will harden and gain strength over time. Unlike Type F, self-cementing Type C fly ash does not require an activator. Alkali and sulfate (SO_4) contents are generally higher in Type C fly ashes. Type C will generate more heat of hydration than Type F. Type C ash will generate more strength at early ages than Type F [265].

Fly ash is widely employed as a superior substitute for Portland cement in the construction industry, primarily because of its pozzolanic and cementitious properties [257]. Fly ash typically replaces around 20% to 30% of the total Portland cement used in construction activities [218]. When added to concrete, the properties of HCFA improve by: (i) high strength, (ii) higher durability (iii) relative lower drying shrinkage, (iv) reduced heat of hydration, (v) reduced sulphate attack and reduced efflorescence, (vi) decreased permeability, (vii) higher setting time. Furthermore, the workability improves by: (i) light weight concrete, (ii) improved, (iii) reduced segregation and bug holes, (vi) reduced bleeding, (vii) less sand needed in the mix to produce required workability [260].

Fly ash utilization

There are many applications for the use of fly ash, this means that the characteristics of fly ash need to be diverse and fit the required chemical process in order to obtain the final carbon-base product. Some of these applications are; cement and concrete (utilizes around 45% of the global fly ash market share), fills & embankments, waste stabilization, mining, oilfield services, and road stabilization Figure 47 and Figure 48. Furthermore, the most utilized applications are [264]:

1) Structural fill applications rest primarily on the ability of the material to be compacted to a reasonably strong layer of low unit weight. This is primarily a function of particle size distribution, and to some extent of the content of spherical particles. The chemical characteristics of fly ash are secondary, although the post compaction cementation provided by some high-calcium fly ash is likely to prove beneficial.

2) Highway applications require that chemical considerations come into play, however, this is not the most important requirement. Stabilization of some base courses (and stabilized sub grades) may rest on lime fly ash chemical reactions, i.e., the classical ‘‘pozzolanic’’ reaction, with lime. Nevertheless, the most important chemical requirement for highway applications is that fly ash contains sufficient so that it can react with the lime. Some road base applications of fly ash depend on the physical effects of fly ash incorporation rather than its reaction with lime.

3) Fly ash used as raw material for cement and concrete applications post the greatest demand. The required characteristic is uniformity and chemical consistency of the raw material (i.e., need for consistency regardless of the days the fly ash is collected).

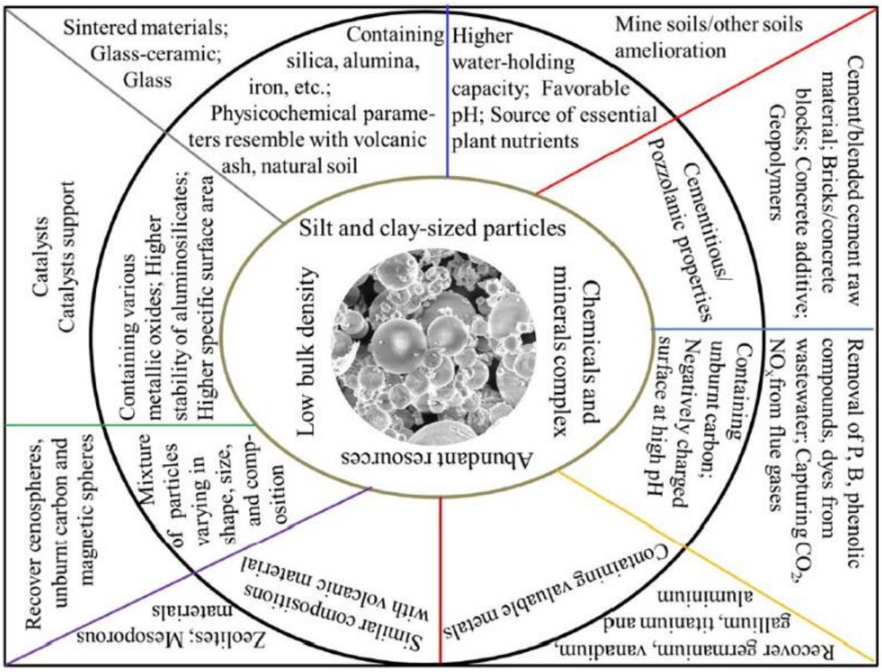


Fig. 47. Various possible utilization of fly ash [266]

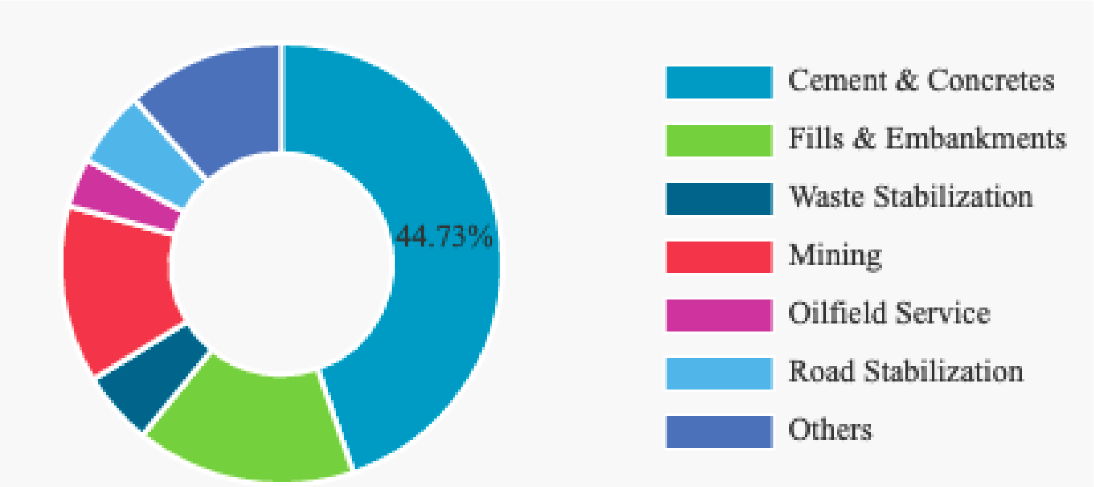


Fig. 48. Global Fly Ash Market Share, by Application, 2019 [267]

Fly ash typically replaces around 20% to 30% of the total Portland cement used in construction activities [268]. The need for infrastructure has been increasing at significant pace due to the rapid growth in global population, especially in developing countries such as China and India. This has led to an increase in construction activities throughout the globe.

Fly ash is extensively used in the construction industry as an environmentally sustainable substitute for Portland cement. However, lack of global awareness about the benefits of using fly ash as construction material is hindering the fly ash market. Furthermore, the sector is controlled by a few of major producers, which are careful about pioneering new products that contest their current business models. In the lack of a strong carbon-pricing indication, there is minimum short-term economic incentive to make changes [269]. Unconventional materials are often not readily available at the scale required. Meanwhile, architects, engineers, contractors and clients are justifiably cautious about innovative building materials. Implementing novel practices also indicates a critical role for millions of workers involved in using concrete across all spectrums of the market [270].

Coal Power Plants and CO_2 emissions in U.S., E.U, and China

The number of plants newly under construction each year is falling even faster, down 66% in 2019 compared to 2015, according to the latest annual status report from Global Energy Monitor [271]. Meanwhile, coal retirements are at historically unprecedented levels, with the 34GW of closures in 2019 a close third behind 2015 (37GW) and 2018 (35GW) [268].

Some 80 countries use coal to generate electricity, up from 66 in 2000. Since then, 15 countries have added coal capacity for the first time and one country; Belgium has phased it out [272]. Another 19 countries, responsible for 5% of current capacity, have pledged to phase out coal as part of the “Powering Past Coal Alliance” [273], led by the UK and Canada. This now officially includes Germany, home to the world’s fifth-largest coal fleet and some 2% of the global total [274].

Since 2000, the most dramatic changes have taken place in China. Its coal fleet grew five-fold between 2000 and 2019 to reach 1,005GW, nearly half the global total [275]. China is the world’s largest CO_2 emitter and uses half the coal consumed each year, so its future path is disproportionately important for global efforts to tackle climate change [276].

A wave of retired power plants has cut US coal capacity by 105GW since 2010 and another 71GW is already planning to close, according to Global Energy Monitor. This would shrink the US fleet by half, from 327GW in 2000 to 175GW in 2024 [277].

Global CO_2 emissions declined by 5.8% in 2020, or almost 2 Gt CO_2 – the largest ever decline and almost five times greater than the 2009 decline that followed the global financial crisis [278]. Despite the decline in 2020, global energy-related CO_2 emissions remained at 31.5 Gt, which contributed to CO_2 reaching its highest ever average annual concentration in the atmosphere of 412.5 parts per million in 2020 [279] – around 50% higher than when the industrial revolution began [280].

Global coal use is expected to rebound in 2021 and drive an increase in global CO_2 emissions of around 640 Mt CO_2. This would push emissions from coal to 14.8 Gt CO_2: 0.4% above 2019 levels and only 350 Mt CO_2 short of the global high in coal-related CO_2 emissions of 2014 [278]. The power sector accounted for less than 50% of the drop in coal-related emissions in 2020, but it accounts for 80% of the rebound, largely due to rapidly increasing coal-fired generation in Asia [276].

China’s emissions are likely to increase by around 500 Mt CO_2. With energy demand and emissions already growing in 2020, in 2021 CO_2 emissions in China should be 6%, or almost 600

Mt CO_2, above 2019 levels [278]. All fossil fuels should contribute to higher CO_2 emissions in China in 2021, but coal is expected to dominate, contributing 70% to the increase, predominantly due to greater coal use in the power sector. Despite China's rapid growth in generation from renewables, output from coal-fired power plants has increased by 330 TWh, or nearly 7%, between 2019 and 2021 [281].

In the United States, CO_2 emissions in 2021 are expected to rebound by more than 200 Mt CO_2 to 4.46 Gt CO_2 yr. remain 5.6% below 2019 levels and 21% below 2005 levels. CO_2 emissions from coal are expected to be almost 12% below 2019 as coal use for electricity generation is likely to recover only 40% of the ground lost to renewables and natural gas in 2020 (Fig. 49). Oil use, the biggest contributor to CO_2 emissions in the United States, should remain almost 6% below 2019 levels as transport activity remains curtailed across 2021 [282].

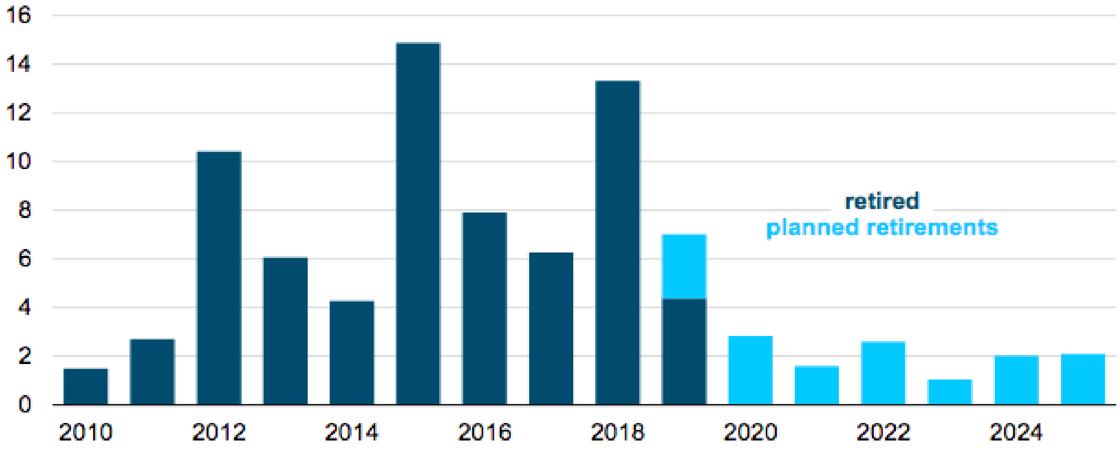


Fig. 49. Total net summer capacity of retired and retiring coal units U.S. (2010-2025) [277]

CO_2 emissions are likely to rebound less in the European Union, as the economic outlook is dimmer than in other parts of the world. The expected increase of 80 Mt CO_2 in 2021 will reverse only one-third of 2020's drop [283]. EU emissions in 2021 should stand at 2.4 Gt. Most of the 90 Mt CO_2 drop in power sector emissions in 2020 will endure through 2021, with a slight anticipated increase in coal and gas-fired generation in 2021 reversing only 10% of the 2020 drop. The share of coal in electricity generation in the European Union has declined almost three-percentage points from 2019 to 2021, to less than 14% [278].

CO_2 emissions from advanced economies have fallen by 1.8 Gt CO_2 since 2000, and their share in global emissions has declined by twenty percentage points to less than one-third of the global total [269].

Poland, the Czech Republic, Romania and Bulgaria continue to depend heavily on lignite power. Plans for a phase-out are crucial if the European Union is aiming to abide with the Paris Agreement. Such plans are necessary not only to create a coal-free EU but also because lignite power plants have swung from being an asset to a liability as lower electricity price and higher carbon prices have crushed their economies [284].

Nevertheless, Poland has moved closer to ending reliance on coal after the government, the country's largest mining firm and unions agreed to phase out all coal mines by 2049. It was the first time Poland has put a timeline on ending coal and puts the country in line to meet EU's climate target of net-zero carbon emissions by 2050, which had previously been rejected by Warsaw as unrealistic.

A big motivator was the "Law and Justice (PiS)-led government" was forced to shift its position due to the rising costs of emissions permits required within the EU's cap-and-trade system and the effects of the Covid-19 pandemic, which has reduced demand for electricity and exacerbated a long-term structural decline in prices [285].

The country generates about 75% of its electricity from coal — second only to Germany in Europe and making Poland the ninth-largest coal producer in the world. The new plan foresees renewable energy sources accounting for at least 32% of electricity by 2030 [284].

CCP Production and Utilization in the U.S. and EU

Coal combustion products (CCPs) include combustion residues such as boiler slag, bottom ash and fly ash from different types of boilers as well as desulphurization products like spray dry absorption product and FGD gypsum [286]. CCPs are mostly used in the building material industry, road and underground coal mine construction, recultivation and restoration purposes in open cast mining. In most cases CCPs are used as a replacement for natural materials; consequently, contributing to the sustainable development of environmental activities by avoiding the need to quarry natural resources. Furthermore, CCPs helps reduce energy demand as well as CO_2 emissions generated by the manufacturing process of the products which are replaced, and they lead to energy savings when used in mixtures with wet raw materials.

The CCP production worldwide is estimated to be around 700 million tones (MT), with fly ash constituting about 75–80% of the total ash produced; approximately, 80% Type F and 20% Type C [287]. In Europe, over 40 MT of CCP is produced [288] and approximately 27 MT is of fly ash utilized [289]; however, a significant amount of ash is still expected to be disposed of in landfills [290]. A large fraction of the coal ash in the world, about 70% of the total production, is typically disposed of as a waste in utility disposal sites [291].

In the United States, around 79 MT of CCP is produced by coal-burning power plants and 41 MT is utilized [4].

According to the American Coal Ash Association (ACAA), fly ash use in concrete increased slightly as overall coal ash recycling rate decline in 2019 [292].

Fifty-two percent of the coal ash produced during 2019 was recycled –marking the fifth consecutive year that more than half of the coal ash produced in the United States was beneficially used rather than disposed. The volume of fly ash used in concrete increased 1 percent over the previous year, but most other uses saw significant declines, leading to an overall decrease in recycling activity of 31 percent [207]. Forty-one million tons of coal combustion products were beneficially used in 2019 out of 78.6 million tons that were produced. The rate of ash utilization decreased from 58.1percent to 52.1 percent and the total volume of material utilized decreased by 18.4 million tons compared to the previous year. Coal ash production volume decreased 23 percent (or 23.6million tons) from 2018 levels [293]. Some examples as it relates to the utilization of fly ash in the cement production and pond closure activities are [207]:

Regulatory framework in EU and US and fly ash management

5.6.1. Fly ash management

Managing large quantities of fly ash is a concern for every developed nation in the world, the unease intensified by the extensive range of chemical and physical properties that fly ash exhibits. Operators of coal-fired power plants must manage costs, revenues, and risk to be prosperous. Successfully managing fly ash has become a progressively important piece of total success for power plants. In the fly ash/cement/concrete/construction business environment, power plants must carefully control expenses, capital commitments and risks and smart management of coal combustion products provides a significant opportunity in several important ways: [294]

- Cost reduction and cost management for landfill: managing fly ash results in landfill cost avoidance by reducing current ash disposal expenses and by delaying or avoiding the significant costs of future landfill or pond development.
- Evading or Reducing Future Liability: recycling fly ash means reducing the chances that, in the future, environmental regulators will take actions aimed at a fly ash disposal site.
- An Environmentally Friendly Solution: beneficiation and utilization of fly ash is a “green” solution that turns expenses into revenue and demonstrates a utility’s commitment to the environment and the communities in which they do business

For fly ash to gain acceptance by potential users, it must not only be available economically, but at a uniform quality as well. The physical properties and chemical composition of fly ash produced by each coal-burning power plant is dependent upon the characteristics of the coal that is used as fuel, the type of equipment employed, and the way it is operated and maintained. Since these characteristics vary from plant to plant, from country to countries, and from local communities- it is not unexpected that fly ash properties vary from source to source. In addition, fly ash collected at any one source will change as the demand on the power plant varies from base to peak loading conditions and as conditions within the producing plant change. These considerations, as well as the fact that coal-burning electric utilizes are primarily concerned with the production and sale of electric power, contribute to the difficult in producing a fly ash of uniform quality. Added to this is the further obstacle that each product with fly ash utilization potential has individual quality requirements [295].

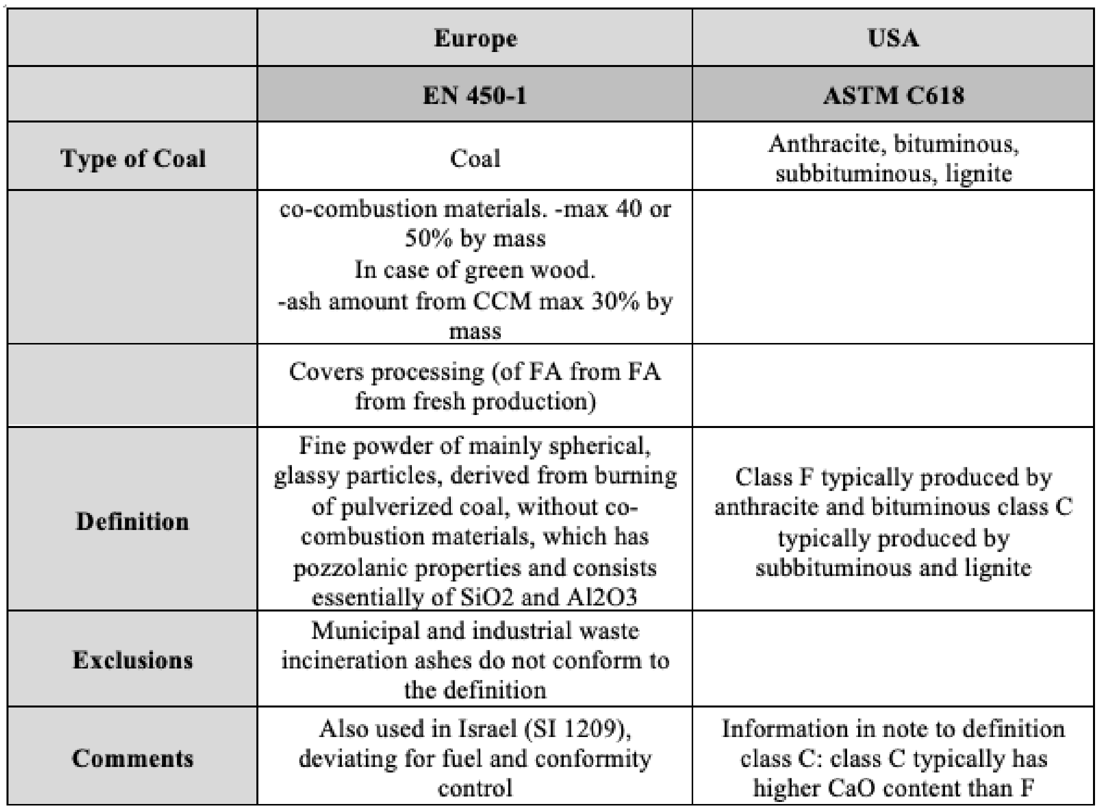
Cement with fly ash additive must be marketed as a separate product, and as such, separate handling, storage, stocking, etc., are involved [296]. Also, the blending of the two materials requires special techniques to ensure uniformity of the cement. The economics of handling and transportation do not allow for the mass utilization of fly ash in this manner without the combined cooperation of power plants and Portland cement producers [295].

5.6.2. Fly ash regulatory framework- U.S. and E.U.

As the use of CCPs is either standard or project related the national regulations for the use in different applications must be considered. Basically, all standards deal with fly ash or pulverized fuel ash from coal (Europe, Australia/New Zealand and Japan), specifically anthracite, bituminous, subbituminous and lignite (USA, India and China) or also blended coal mixtures (Russia) [297]. These standards contain chemical and physical properties of the ash. It must be noted that the standards are used in combination with application standards and other regulations, including environmental requirements [298].

Only the European Standards cover co-combustion of defined materials in specific amounts to ensure ashes characteristics are within a defined range. In addition, processing is covered for ashes which basically follow EN 450-1 standard except for fineness and LOI. Ashes can be processed in suitable production facilities through classification, selection, sieving, drying, blending, grinding or carbon reduction, or by a combination of these processes [259]. Such processed fly ash may consist of fly ashes from different sources, each conforming to the basic definitions required to meet the criteria of the standard. South Africa uses the EN standard in full and Israel has implemented it with minor deviation by exclusion of co-combustion and quality control systems Table 14 [2].

Table 14. Typical Properties of International Standards [299][259][2]



	Europe	**USA**
	EN 450-1	**ASTM C618**
Type of Coal	Coal	Anthracite, bituminous, subbituminous, lignite
	co-combustion materials. -max 40 or 50% by mass In case of green wood. -ash amount from CCM max 30% by mass	
	Covers processing (of FA from FA from fresh production)	
Definition	Fine powder of mainly spherical, glassy particles, derived from burning of pulverized coal, without co-combustion materials, which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3	Class F typically produced by anthracite and bituminous class C typically produced by subbituminous and lignite
Exclusions	Municipal and industrial waste incineration ashes do not conform to the definition	
Comments	Also used in Israel (SI 1209), deviating for fuel and conformity control	Information in note to definition class C: class C typically has higher CaO content than F

The definitions all address the collection of fly ash from the flue gas by electrostatic precipitators or other collection methods. They address siliceous and/or calcareous ash (Europe, Japan, India, Russia) or Class F and Class C depending on the coal burned in the USA and China. Characterization of calcareous (class C) fly ash from siliceous (class F) requires that the amount of reactive calcium oxide in the Class C ash is greater than 10% [299][2][259].

In Europe, the cement standard EN 197-1 defines two types for calcareous fly ash: a W1 class with reactive lime content of 10 to 15 % and reactivity test as for siliceous type ash; and a W2 class with more than 15 % of reactive lime considered as a binder with own compressive strength requirement [259] [269]. In addition, there are rules for consideration higher Sulphur contents. The chemical and physical requirements of the standards are compiled in Table 15 based on their reactive evaluation for siliceous (Type F) or calcareous (Type C).

Table 15. Scope and definitions of EU and USA used standards for fly ash in concrete and cement [249][259]

PROPERTIES OF FLY ASH	ASTM C618		EN 450
Chemical Properties	**Class F**	**Class C**	
$SiO_2 + Al_2O_3 + Fe_2O_3$ (min. %)	70	50	70
Sulfur trioxide (SO_3) (max. %)	5	5	3
Moisture content (max. %)	3	3	-
LOI (max.%)	6	6	-
Silicon dioxide SiO_2 (max. %)	-	-	25
Relative silica by mass (max. %)	-	-	-
Magnesium oxide MgO (max. %)	-	-	-
Alkalies Na_2O (max. %)	-	-	-
Chlorides Cl (max. %)	-	-	0.1
Total/reactive CaO (max. %)	-	-	10
Physical Properties			
Fineness:			
Amount retained when wet-sieved 45μm (No.325) sieve, (max.%)	34	34	40
Specific surface (m2/Kg) (min.) (Blaine's Permeability method)	-	-	-
Strength activity index:			
With Portland cement, at 7 days (min. % of Control)	75	75	-
With Portland cement, at 28 days (min. % of Control)	75	75	75
Lime Reactivity (Avg. Compressive StrengthMpa) (min.)	-	-	-
Water requirement (max. % of control)	105	105	-
Specific Gravity	-	-	-
Soundness:			
Autoclave expansion or contraction (max. %)	0.8	0.8	-
Uniformity requirements:			
Density (max variation from avg. %)	5	5	-
Percent retained on 45μm (No.325) (max, variation % from Avg.)	5	5	-

Another difference between ASTM C618 and EN 450-1 that is worth mentioning relates to the disposal of fly ashes in landfills. In the United States, bottom and fly ashes from coal power plants are typically mixed before the disposal into landfills to meet the U.S. Environmental Protection Agency (EPA) requirements. Conversely, in many European countries, the fly ash is not mixed with bottom ash but rather handled as a special waste. In this instance, the bottom ash is often recycled and used as a material in pavement and other similar products [300]. To simplify the efficient use and disposal of fly ash, regional authorities around the world have developed a variety of classification strategies. Most fly ash end-users are only interested with the local specifications. The selection of fly ash is generally predicted upon the expense of transporting the ash that meets the minimum criteria for the project, a practice that is not likely to change in the immediate future [301].

ASTM C618, ASTM 311, and AASHTO M 295 specifications for fly ash represent the primary documents used by U.S. state and federal agencies to determine the suitability of a fly ash source for use in concrete. Other countries have broadly similar specifications for fly ash. As recent as the first quarter of 2021, the ACI (American Concrete Institute), published a document [299] where it compares specifications from the United States, Canada, Europe, Australia, and New Zealand, noting similarities and differences. Despite its common use, several criticisms of the ASTM C618 specification exist and are discussed in the document. Specifically, concerns exist regarding its dependence on strength activity index testing for determination of fly ash reactivity and strength generation potential, and loss on ignition for quantification of unburnt carbon content, as these tests relate somewhat poorly to performance of the fly ash in concrete. Recently developed test methods that could improve some of the most problematic components of the ASTM C618 specification are discussed [299].

In the U.S., an assessment of the impact of existing specifications on the extent of fly ash utilization involves some vague parameters, and credible and meaningful information is not always available. User attitude is a consideration. There have been occasions where if sufficiently motivated, a user can circumvent a provision in a specification, either by allowing an exception, or sometimes by writing their own specification, or by altering a specification. This suggests a basic inadequacy in the current specifications. On the other hand, European standards and testing requirements are more restrictive than similar standards in the US; all applications are not needing standardized concrete, and the potential utility of the studied fly ash materials could be improved by mechanical treatments. Furthermore, implementing these standards in Europe tend to be more successful than in the U.S.; mainly because they are more detailed and better monitored than the standards in the U.S.

5.6.3. High Calcium Fly ash regulatory framework- U.S. and EU

High Calcium Fly Ashes are reactive materials that often do not meet the limits of some countries national and local standards. Therefore, most of the lignite coal produced around the world have not been fully exploited. As previously mentioned, the classification of fly ashes is deeply correlated with the type of coal that is burnt, many efforts are being taken to develop a “standardize” specification that can be used in many global applications. However, because of dissolute experiences when utilizing HCFA in certain applications, efforts of standardization has been delayed [302].

The resources of high calcium fly ash are large, however, this type of ash is usually described by low silica content, a high content of free lime and an increased content of sulfur compounds [303]. It could be used in concrete following the requirements of ASTM C618, Class C, but in Europe, it does not meet the requirements defined in standard EN450-1 [304]. At the moment, HCFA is not in common use in European countries despite positive examples of its suitability provided by Greek and Turkish researchers [213].

When HCFA is used as a complementary cementitious material it can augment some of the physical, behavioral, and structural properties of the concrete (e.g., compressive strength, workability, etc.) [221]. However, the possibility of using HCFA as concrete additive is not well established, especially in relation to the durability of concrete structures in aggressive environment [305]. Due to the high content of lime, HCFA cannot be used to a big extent for building purposes and is currently collected in storage ponds [306].

In 2019 the United States mined and burnt 53 MT of lignite coal, or 8% of the total coal production of the country. Additionally, 44% of coal was subbituminous; 48% was bituminous, and <1% was Anthracite [307]. Consequently, the type of fly ash generated was mostly Type F. However, Type C is also widely available given that 44% of the fly ash produced is generated by the combustion of subbituminous coal. Currently in the U.S., more than 50% of the concrete placed contains fly ash. Furthermore, the most utilized type of fly ash for admixture is Type F.

According to ECOBA [289], the amount of HCFA produced in Europe is more than 50% of the total fly ash generated by burning hard coal and lignite [289]. In the EU lignite coal is the most predominate type of coal used at coal power plants, especially in countries such as Poland where almost all the coal burnt is lignite; consequently, the type of fly ash generated is mostly Type C. Nevertheless, the lack of standards for its utilization has negative impact for the economy and the environment [308].

The most widely known standards in the U.S., for the use of FA and HCFA as a supplement of cement to produce concrete is ASTM C618 [249]. Unfortunately, this specification does not clearly address the use of HCFA in cement/concrete applications. In recent years, regulatory entities have been revising construction codes, standard, and specifications with the goal of improving the clarity of the requirements and making them more detailed in order to avoid many loopholes that are present in the current standards.

The USA standard references that the amount of lime of Class C is typically higher. Though recently being published the standard is again under revision where the lime content in the ASTM standard will be defined to 18 % [299] [299]. With this it is questioned whether the lime levels and related experiences can be associated as the lime content in class F may have been more than 10 % and only the reference to the used coal may be valid for this.

As part of the ASTM revisions, one of the main subjects is addressing changes to ASTM C 618 to classify fly ash by calcium oxide content rather than the sum of the oxides. Going forward, fly ash with a calcium oxide content of 18% or less will be classified as Class F and above 18% as Class C. The American Association of State Highway and Transportation Officials (AASHTO) approved this change in their M 295 specification [309].

Below are some additional C 618 specification developments underway at ASTM:

- a new Class B on the use of milled bottom ash in concrete
- blending of in-spec and out-of-spec fly ash
- blending of Class C and Class F fly ash
- blending of fly ash, natural pozzolans, and other materials to create a new SCM

In Europe there is the EN450-1 for the use of siliceous fly ashes in concrete. However, when assessing specifications for HCFA(s), there is no general existing regulation level for the utilization of this waste in concrete [310], but their use in blended type cements is covered by EN197 Standards [311]. The other Standards that refer or allow the use of HCFA(s) are the EN13282 about Hydraulic Road binders and EN14227 about hydraulic bound mixtures [312], [313].

5.6.4. Mineral carbonation of High Calcium Fly

A possibility to valorize such waste materials is to reduce their total lime content through mineral carbonation techniques. Recent experiments on accelerated carbonation of HCFA under dry and moist conditions, at various temperatures, pressures and compositions, show that the mineral carbonation of a variety of HCFA (with up to 35 wt.% bulk CaO) can reach very high efficiencies under industrial flue gas conditions [7]. Another study performed by UCLA show that HCFA that reacts with CO_2 in moist environments, at ambient pressure, and sub-boiling temperatures, produce robustly cemented solids whose properties are enough for use in structural construction [16].

5.6.5. Market considerations for carbonated fly ashes

Construction materials including Portland cement, concrete, and mineral aggregates comprise the largest material flows in the world, second only to water. Each year, nearly 30 billion tons of concrete [314] are produced globally from a production base of 4.1 billion tons of Portland cement [315]. Given the scale of these markets, mineral carbonation products may have the potential to utilize up to 1 gigaton (Gt) of CO_2 annually if they were to replace existing products [11].

According to Villere, the large production volumes offer substantial economies of scale for conventionally produced products, resulting in costs on the order of $50 per ton for concrete [316] $100 per ton for Portland cement, and $10 per ton for aggregates [317]. Taken together, these numbers define a cost basis for both existing and emerging construction materials. They also highlight some of the challenges that any new product might face: competition with well-entrenched products with low costs that can be produced worldwide [75].

Whilst the construction sector offers large material movements cumulatively, the manufacture of construction materials is a localized activity. For example, in the U.S. there are 5,500 ready-mix concrete plants, [318] hundreds of precast concrete plants, [319] and nearly 100 Portland cement production plants [320]. This localization and fragmentation imply that if mineral carbonation is to be used to produce construction materials that can replace existing materials; (i) CO_2 will need to be consumed

in many discrete locations to produce a range of materials and products, and (ii) the logistics of CO_2 access and transportation of manufactured products will be critical for economic viability [75].

There are many efforts under way to manufacture construction materials via mineral carbonation. Most are being commenced by startup companies and precommercial entities, which fall into two groupings: (i) those producing binding agents in concrete (examples include Solidia Technologies, Carbon Upcycling UCLA, CarbonCure, and Carbstone Innovation) and (ii) those producing synthetic aggregates (examples include Carbon8 Systems and Blue Planet) [77].

Each of these approaches maximizes the use of the thermodynamic ease of mineral carbonation and the potential for cementation offered by calcium carbonate. Though, these activities are in the early stage, they underline the potential for CO_2 utilization in the construction materials markets. Conversely, the scalability and market viability of these approaches are influenced by various factors: (i) the purity and the availability of CO_2, (ii) the availability of low-cost alkaline reagents and/or facilities for their manufacture at scale, (iii) the low-cost, commoditized nature of the existing analogous products, Portland cement and concrete, (iv) limiting building codes and standards wherein compliance is often a function of the material composition (e.g., cement-based chemistries) rather than their engineering performance, and (v) the net amount of CO_2 utilization that can be achieved [75]

In order to develop the market for carbonated fly ashes, the matter of construction codes and standards need to be addressed. In general, it is desirable that a new product achieves performance equality, or idyllically performance benefits, when compared to the product that it will be replacing. While this reasoning makes sense for a vast number of applications, in construction, the line becomes a bit blurred. This is because the construction sector has gained pragmatic confidence in the use of Portland cement and traditional concrete as construction materials, and construction industry standards are infamously slow to change. Furthermore, construction standards and codes are often jurisdictional (e.g., city by city or state by state). This results in fragmented compliance and acceptance standards that may inhibit or delay the market entry and adoption of new products [11]. A further complication is that construction standards are often prescriptive rather than performance based; as such, they often define the compositions of materials that can be used [75]. Pending external forcing through legislation preferential government purchasing programs, or the imposition of CO_2

taxes and penalties, this is a substantial challenge that must be overcome before the use of carbonated materials can become widespread within the construction sector. Among other elements, this requires moving to a system of harmonized performance-based standards, which will accelerate the adoption and acceptance of new materials for construction applications and new tools that can model and predict long-term performance of new materials [75].

Market, Costs, and Policies on CCUS
U.S. vs. EU

As nations grow their energy portfolios, fossil fuels are expected to meet a large part of the world's energy demand for many years. Accelerating deployment and commercialization of carbon capture technology is vital to reduce emissions from carbon fueled power plants, and from industrial plants such as cement, steel, and chemicals manufacturing.

As momentum builds in the global effort to stop climate change, numerous countries are launching transitions to a lower-carbon economy, driving influential investors to look increasingly for resulting opportunities to put capital to work. Subsequently, a pool of patrons and forward-thinking investors are noticing that they can both help the world decrease its carbon footprint and generate a return for their clients through investment tools from carbon capture credits to carbon capture technology and commercialization of carbon-based products. While the transition will happen over decades, now's the time to start thinking about ways to invest in the burgeoning carbon asset class.

In the midst of worldwide COVID-19 lockdowns, the global CO_2 emissions fell to levels that the world has not seen since in decades; moreover, authorities and companies did not dither in their commitment to battle climate change. While this is good news, it also exposes how much more still needs to be done to lower emissions; even with the pandemic, unabetted fossil fuels still provide about 80% of primary energy and global emissions [321].

The year 2020 also saw the increase attention of nations and industries who had pledge to achieve cost-effective net-zero emissions with CCUS by 2050. Furthermore, initiatives such as the Race to Zero and the Climate Ambition Alliance helped mobilized coalitions representing 708 cities; 24 regions; 2,360 businesses; 163 of the biggest global investors; and 624 Higher Education Institutions, to build momentum around the shift to a decarbonized economy ahead of COP26, where governments must strengthen their contributions to the Paris Agreement [322].

Carbon removal with CCS technologies

The task of carbon removal in climate change mitigation1.5°C, compared to pre-industrial levels. The 1.5°C mitigation pathways project carbon removal in the order of 100–1000 gigatonnes of CO_2 over the 21st century [323]. Carbon removal would be used to counterbalance for residual emissions and achieve net negative emissions to limit global warming to 1.5°C. The two elements in the climate change mitigation pathways – emission reductions and removals – are behind the reckoning of net zero emissions, and net negative emissions thereafter. The role of emission reductions and removals in the mitigation of climate change will change over time. It is widely agreed that emission reductions should be prioritized on the pathway to net zero. This, however, will change once net zero emissions are achieved; net zero is a point on the journey, not the final destination. Carbon removal will become the main driver of climate ambition in the second half of the century [324].

6.1.1. What does carbon removal mean?

There is no general established definition of carbon removal. “Carbon removal” is used to describe approaches that can remove CO_2 from the atmosphere and store it away permanently. Other terms like “greenhouse gas removal” (covers CO_2 and other GHGs) or “negative emissions” are often used in the same context. However, negative emission technologies (NETs) are sometimes used interchangeably with carbon removal. Whether a NET delivers carbon removal, depends on the details of how it is used in practice, as described in the list below [324].

There is a list of four criteria that could be used to determine whether a climate solution or technology can deliver greenhouse gas removal [325].

- Physical greenhouse gases are removed from the atmosphere.
- The removed gases are stored out of the atmosphere in a manner intended to be permanent.
- Upstream and downstream greenhouse gas emissions associated with the removal and storage and included in the emission balance.
- The total quantity of atmospheric greenhouse gases removed and permanently stored is greater than the total quantity of greenhouse gases emitted to the atmosphere.

The twofold task of CCS in climate change mitigation

CCS technologies have a dual role in climate change mitigation. First and foremost, CCS technologies can reduce emissions from energy intensive industries and power generation. Secondly, CCS technologies can be used for carbon removal from the atmosphere. The main applications for emission reductions and carbon removal are as follows [326]:

6.3.1. Reducing emissions

- Decarbonization of heavy industry, most notably reducing emissions from the production of cement, steel and chemicals. These sectors are amongst the hardest to abate due to their inherent process emissions and high temperature heat requirements. CCS provides one of the most mature and cost-effective options for reducing emissions from these sectors.

- Clean hydrogen production by contributing as an enabler of the hydrogen economy via blue hydrogen production.
- Reducing emissions from recently built power plants, in particular coal and gas facilities in Asia [327] CCS provides the foundation for technology-based carbon removal, including BECCS and DACCS [328]. BECCS includes the conversion of biogenic Waste-to -Energy with CCS which reduces landfill and methane production, and which does not require additional production of biomass.

Circular Carbon Economy

The concept of a Circular Carbon Economy (CCE) was developed by King Abdullah Petroleum Studies and Research Center (KAPSARC) helps to address this risk by creating a framework that recognizes and values all emission reduction options [329]. The CCE builds upon the well-established Circular Economy concept, which consists of the “three Rs” of Reduce, Reuse and Recycle, works well in describing an approach to sustainability considering the efficient utilization of resources and wastes, but has proven manifestly inadequate as a framework for defining climate action. To be effective, a fourth R must be added; Remove, creating a new concept the Circular Carbon Economy (CCE) [330]. The CCE provides for the removal of carbon dioxide from the atmosphere (Carbon Direct Removal or CDR) and the prevention of carbon dioxide, once produced, from entering the atmosphere using carbon capture and storage (CCS) [331]. The CCE establishes a framework that respects the analysis of the Intergovernmental Panel on Climate Change (IPCC) and many others, that all conclude that CCS and CDR, alongside all other options, are essential to achieve climate targets [332].

Measures taken under the Remove dimension of the Circular Carbon Economy contribute to climate mitigation by storing carbon dioxide in the geosphere (CCS or DAC with geological storage) or in the biosphere (nature-based solutions such as afforestation). However, CO_2 stored in the biosphere via nature-based solutions may be susceptible to release due to natural phenomena such as fires, droughts or disease (of plants). Technology-based solutions such as CCS and DAC with geological storage offer extremely secure and permanent storage of CO_2, which is not susceptible to disruption from fire or weather, as well as requiring very little land for facilities with a capacity to provide multi mega-tonne per annum abatement [333].

In recent years, climate change mitigation and adaptation efforts and treaties such as the Paris Agreement have led to financiers and investors including the environmental and social impact of companies in decision making processes. At the same time, businesses across sectors are searching for ways to stay competitive while improving their environmental and social impact [334].

The circular economy is an economic system that combines economic, environmental and social prosperity. Circular businesses typically employ strategies that aim to extend the lifespan of products and materials for as long as possible, at their highest value. Waste is designed out of the system by using resources in cyclical ways. Moreover, the circular economy assumes the use of renewable energy for production processes and aims to foster social inclusivity [334].

Implementing circularity in business activities essentially entails incorporating externalities (i.e., impact) in the business and revenue model. Compared to their linear counterparts, circular companies may have a lower financial performance, due to the costs incurred for activities that have a positive economic, environmental or social impact. Therefore, in striving for a fair assessment of a company's performance, it is key to create a level playing field and rate all companies the same way. This requires different information and different assessment frameworks. Here, circular Impact measurement can offer a solution. In addition to the financial management information provided in financial statements, companies and financiers are looking for additional information with which they can optimize business operations and better estimate risks. Relating circular impact to financial impact can enable more substantiated decision-making and unveils a company's license to operate [334].

CO_2 utilization and storage pathways

The capture and utilization of CO_2 to produce valuable products may diminish the net costs of reducing emissions or removing CO_2 from the atmosphere. This section looks at various pathways for the utilization of carbon dioxide. CO_2 utilization often indicates manners to reduce the net costs—or grow the profits—of reducing emissions or removing CO_2 from the atmosphere, in other words, it's a way to support the scaling of mitigation or removal efforts [90]. CO_2 utilization is frequently viewed as a steppingstone towards or a distraction away from the successful realization of CCS at scale [335].

There is a wide array of carbon utilization options (Fig. 50), each carbon utilization pathway has specific characteristics in terms of technical maturity, market potential, economics, and CO_2 reduction impact. Given this diversity, implementing both broad-based policies and sector-specific ones together will have the greatest impact on CCU development [83].

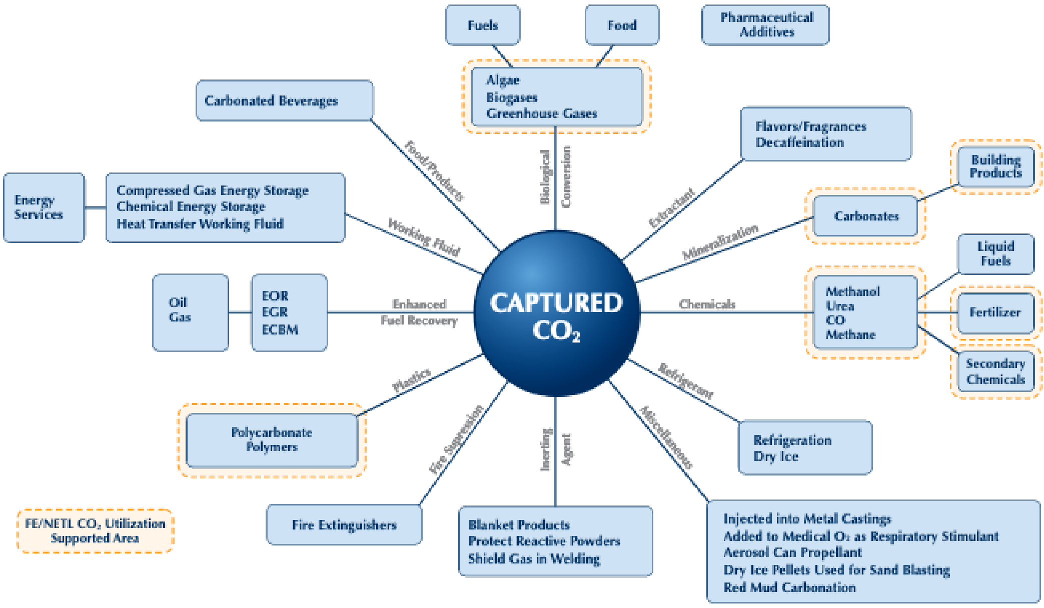


Fig. 50. Stocks and net flows of CO_2 including potential utilization and removal pathways [336]

CO_2 utilization, storage, and the carbon cycle

The amount of carbon dioxide that is utilized by a pathway is not necessarily the same as the amount of carbon dioxide removed or carbon dioxide stored. CO_2 utilization does not necessarily reduce emissions and does not necessarily deliver a net climate benefit, once indirect and other effects have been accounted for. The various concepts overlap and relate to each other, however, they are very distinct from each other. Some CCU processes achieve carbon dioxide removal (CDR) from the atmosphere, and some involve CCS. CCS itself can contribute either to the mitigation of CO_2 (e.g., by reducing net emissions from a gas-fired power plant) or to atmospheric removals (e.g., by direct air carbon capture and storage, or DACCS); CCS does not necessarily imply CDR. Furthermore, CCS and CDR can fail to deliver a climate benefit [83].

For CO_2 utilization to contribute usefully to the reduction of atmospheric CO_2 concentrations, the scale of the pathways must be meaningful in comparison with the net flows of CO_2 shown in Fig. 52. The flow of CO_2 through the different utilization pathways can be represented by a combination of different steps (labels A to L; Fig.3, Table 1). Utilization pathways often involve removal (A or B) and storage (D, E or F); however, the permanence of CO_2 storage varies greatly from one utilization pathway to another, with storage timeframes ranging from days to millennia [83].

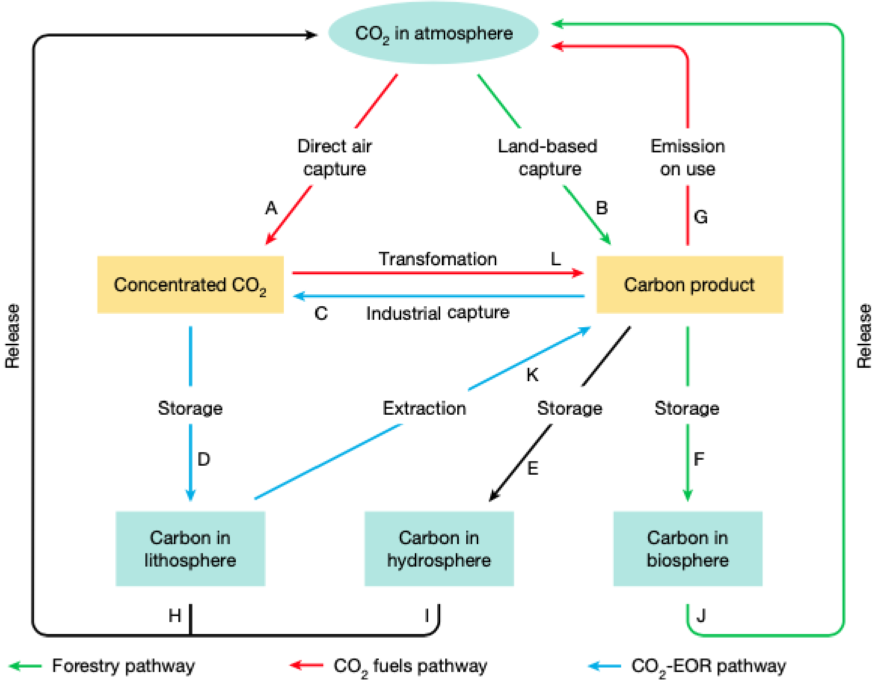


Fig. 51. Carbon dioxide utilization and removal cycle [83]

Cost of Carbon Capture

The cost of capturing CO_2 from power stations has halved over the past decade and the next generation of capture technologies offer further reductions in cost. The lowest cost opportunities for CCS can deliver multi-million tonne CO_2 abatement at a single facility, at a cost of less than USD20 per tonne [337].

CO_2, is significantly more than from industrial point sources. However, the cost is falling and will fall further due, if nothing else, to economies of scale that arise from plant capacities increasing from thousands of tonnes per year to millions of tonnes per year. That cost may be $300 per tonne of CO_2 or less within the next decade. Currently, abatement costs approach or exceed $1000 per tonne for some sectors, and for others, there are no technologies that can reduce emissions to zero [337]

6.6.1 Understanding the cost profile of CCS

The capital cost of CCS often includes investments of billions of dollars, which in comparison to the capital investments of other sources of clean energy, such as wind and solar –both of which are at a smaller scale and require smaller absolute investments –can seem expensive. However, capital costs are not a suitable benchmark to assess whether an emissions reduction technology is expensive because they do not reflect the true cost of reducing emissions. There are different ways to manage the cost of CCS, including for example $/t of CO_2 avoided.

Notwithstanding CCS' flexibility, power generation equipped with CCS, which can be around \$60/tCO_2 [338] when in vicinity to quality geologic storage resources, is frequently used as a singular cost reference for CCS. Furthermore, the levelized cost of electricity (LCOE) is also often cited. However, LCOE fails to account for essential network support and balancing services many of which cannot be provided by intermittent renewables, but which traditional generation equipped with CCS is ideally suited to. Bringing flexibility, dispatchability, reliability, energy security, and low emissions–all important attributes in a net-zero grid penetrated by high-levels of renewables- is a strength of CCS often overlooked as these attributes are not covered by LCOE which neglects to reflect overall system cost [338]. Most importantly, as outlined above, there are various industries which CCS can help to decarbonize, with some of these applications such as natural gas processing, ethanol and, fertilizer production starting at \$20/tCO_2 [338]. As previously mentioned, as a general rule, not all carbon capture applications are created equal in terms of cost (Fig. 53) [338], and the higher the purity of the CO_2 in the flue gas waste stream, the lower the cost to capture.

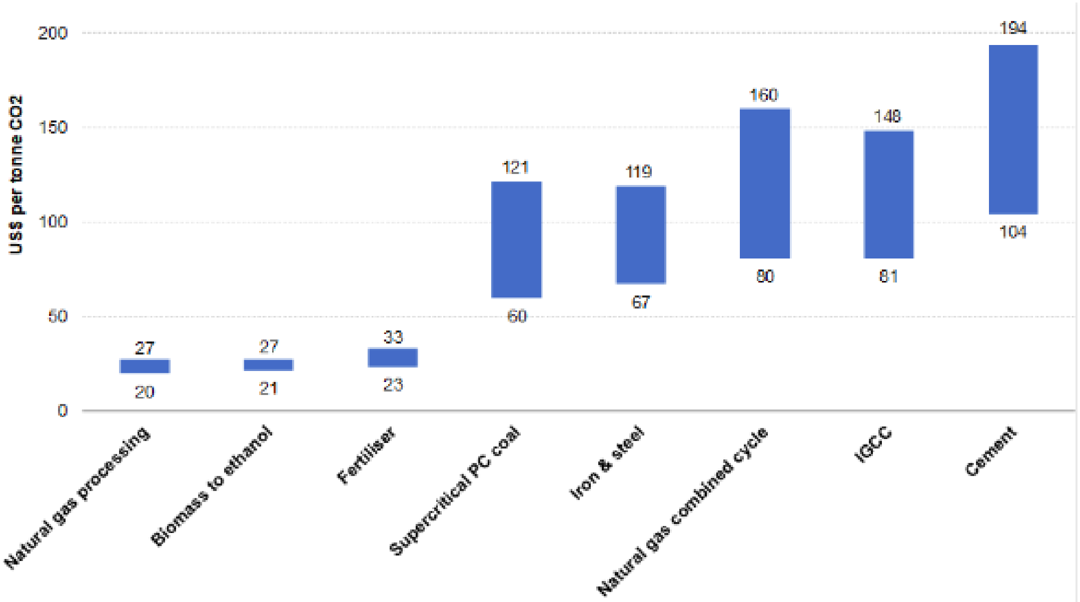


Fig. 52. The cost of CO_2 avoided first of a kind from the Global Cost of CCS [338]

6.6.2. The importance of limiting system cost

To reach global climate goals in line with limiting warming to 1.5 degrees Celsius, the IPCC estimates that an average of \$3 trillion will need to be invested in the energy system each year until 2050 [339] ; about twice as much as current investment. However, there are low-cost and high cost decarbonization on pathways, and analysis has shown that the inclusion of CCS diminishes the overall system cost of decarbonization. For example, the IPCC found that it would be 138 per cent more expensive to reach global climate goals without the deployment of CCS [340]. With regards to

US power grid decarbonization, studies have concluded that the availability of firm low-carbon resources such as natural gas with CCS consistently lowers decarbonized energy system costs, reducing cost up to 60 percent in zero-CO_2 cases [341]. Hence, CCS deployment is vital to a globally equitable and least cost energy transition.

6.6.3. The role of technology deployment in cost reductions

Cost should not be a deterrent to investment. Rather, cost reductions are one of the prime reasons why investment in CCS today is important as the learning that results from deploying CCS will inevitably deliver cost reductions, which can also increase and improve access to the technology globally.

As with many technologies that are not widely deployed, the cost of capital for CCS facilities is currently high. Considering the potentially large amounts of capital investment, high costs of capital are a significant factor driving up overall project cost. However, with increasing deployment the cost of capital is expected to fall (Fig. 54) [338].

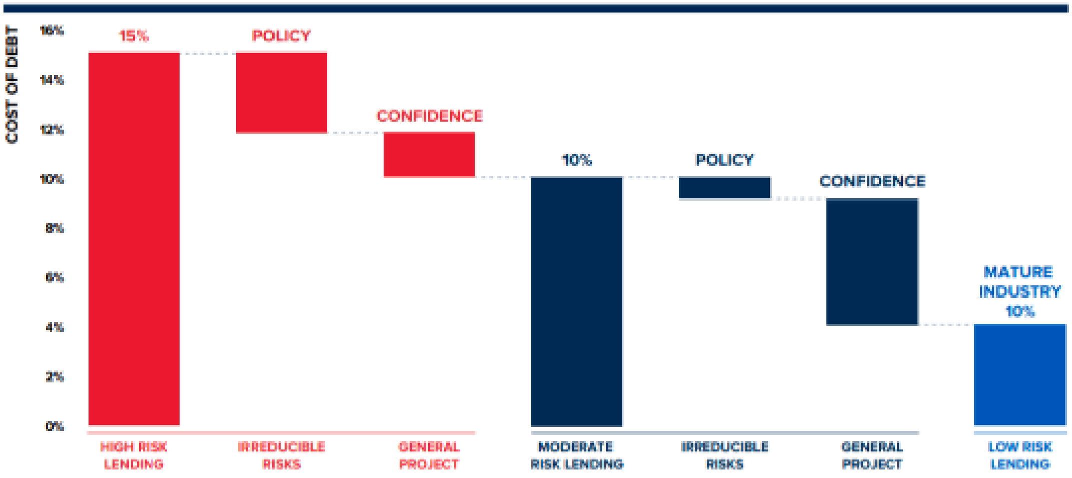


Fig. 53. The Evolution lending rates with policy and increased deployment rates for CCS facilities [338]

Larger average CCS plant sizes, as well as evolving business models such as hubs and cluster approaches where multiple sources of CO_2 share transportation and geologic storage infrastructure are expected to achieve economies of scale and further drive down unit costs. In the meantime, governments and private sector continue to invest in R&D and keep on working on the growth the next generation of technologies that will cut costs even more.

Economies of Scale

In order to realize wide-scale deployment of CCUS, policy incentives are needed [342]. Three primary actions improve the feasibility of wide-scale CCUS deployment: placing a value on

CO_2 through a carbon tax or other policy instrument, lowering risks to investment through financial support from grant funding or other provisions from federal and state government [331] and facilitating the development of CO_2 transport and storage infrastructure [331] [7].

Because fossil fuels are forecast to continue to dominate primary energy supplies, and strong demand for industrial goods requiring high-temperature heat (including cement, steel, and chemicals) persists, CCUS remains an effective tool for policymakers to address climate change problems. To foster industrial scale CCUS development, a carbon tax could be utilized to incentivize CCUS, using its revenues to reduce CCUS costs [343].

Carbon Capture and Storage are essential technologies to help achieve the ambition of net zero anthropogenic greenhouse gas emissions by 2050. As with all solutions, the cost of deployment of CO_2 capture, transport and storage systems is of vital economic and environmental importance. This importance will continue to increase as the scale and breadth of CCS deployment grows around the world. The Global CCS Institute [202] has developed this report to describe the factors that drive current and future costs of the technology. Key drivers of CCS cost include economies of scale (which incentivizes the development of CCS hubs to build scale); partial pressure of CO_2in the source gas (lower partial pressures are more challenging), which mean there is variation in CCS costs from industry to industry; energy costs (in the forms of heat and electricity); and technological innovation [344].

Overcoming the technology ‘valley of death’: The role of a value on carbon

To contribute to emissions reductions at scale and reach climate goals, the deployment of large-scale CCS facilities needs to scale-up 100-fold between now and 2050 [344]. To spur deployment, and to overcome what some refer to as the technology ‘valley of death’–the stage of successful demonstration yet high-capital cost and various factors of uncertainty undermining at-scale deployment –government policy is essential. In addition, as a climate change technology, CCS is deployed only to reduce emissions and for the pure climate benefit. In the absence of a value on carbon that reflects the externalities of emissions, companies will not deploy the technology because there is no incentive to do so [338].

Therefore, a value on carbon is necessary for the large-scale deployment of CCS and to make the business case for deployment. In fact, IEA [7] has estimated that as much as 450 $MtCO_2$ could be captured and stored globally with a commercial incentive as low as \$40/t of $CO_2$by deploying CCS on the many low-cost opportunities available. However, according to the World Bank, 80 per cent of CO_2 emissions are not priced or priced at below \$10/t while the International Monetary Fund suggests it should be around \$75/t of CO_2 [345] to meet climate targets.

There are multiple ways of creating a value on carbon which includes tax credits, like the U.S. section 45Q awards, a carbon market like the European Union Emissions Trading System, and a credit-based system like California's Low Carbon Fuel Standard (LCFS). Mechanisms such as loan guarantees and capital grants that reduce the cost of capital can help lessen overall project cost.

For example, 45Q and the California LCFS CCS Protocol [346] are designed to make the business case for CCS. 45Q will eventually provide \$35/t of CO_2 stored via enhanced oil recovery (EOR) and \$50/t of CO_2 for CO_2 through geologic storage [347]. The California LCFS was trading close to \$200/t of CO_2 in the first months of 2020 [348]. Already, projects that could result in at least a doubling of US CO_2 capture capacity have been announced as a result of 45Q or 45Q and the LCFS, demonstrating that a value on carbon can make an effective business case to deploy CCS [349].

How to accelerate the commercialization of CCS technologies

Technologies develop from initial observations and concepts, through laboratory studies and bench scale equipment, all the way through to pilot-scale and eventually full-scale commercial service.

One of barriers to commercialization is the cost to research, develop and deploy a new technology. However, there are ample opportunities to drive down the cost of carbon capture and to shorten project deployment timelines, through economies of scale, modularization, heat integration, process optimization, combined with next-generation technologies.

Currently, there are many capture technologies in the near-commercial pipeline (e.g., building materials) that could be more cost- effective and efficient in capturing CO_2. All elements of the carbon capture and storage value chain are mature and have been in commercial operation for decades. However incremental improvements in those technologies have and will continue to reduce their cost. For example, the cost of capture from a coal fired power station has reduced by around 50% over the past 10-15 years [344]. Those improvements arise from learning by doing, through competition between vendors, through larger developments that take advantage of economies of scale, and through commercial synergies that reduce the risk and therefore the cost of investing in CCS [350] .

6.9.1. Closing the gap between synthetic fuel and fossil fuel

Achieving the Paris Agreement long-term temperature goal requires closing the ambition and action gap. G20 countries have a crucial role to play in realizing increased climate policy ambition. Synthetic electro fuels (e-fuels) were identified as one of the key policy areas and promising options for intergovernmental cooperation between the G20 nations [351].

The main benefit of fossil fuels versus synthetic fuels is because to their cost advantage on an energy basis. Fossil fuels have an important role in the world economy, it is an incredibly important commodities in the worldwide, leading to a highly competitive environment.

The main environmental problem with fossil fuels is with their combustion process which releases fossil carbon back into the atmosphere, which will become increasingly expensive in a carbon-constrained world.

One area where synthetic fuels have an advantage is being able to help balance the electrical grid, which is likely to suffer from the ever-greater risks of the excess supply of electrical energy [352].

The other important consideration is to account where the carbon itself came from. There should instinctively be a difference if the carbon came from a biogenic source and therefore was already above ground when it was captured by the biomass (thus reducing atmospheric CO_2), as opposed to carbon that was captured from a fossil fuel-based power plant, where the carbon has come from underground. If the fuel is eventually combusted without the carbon being captured again, then the carbon from the biomass can be argued to be rereleased back to the atmosphere without the addition of a further carbon atom. In comparison, if the carbon atom was originally from a fossil fuel source, if the synthetic hydrocarbon is eventually combusted without the carbon being captured again, then this will provide an additional carbon atom into the atmosphere [352].

Carbon Pricing

Carbon pricing is a cost-effective policy tool that governments and companies can use as part of their broader climate strategy [353]. It creates a financial incentive to mitigate emissions through price signals. By incorporating climate change costs into economic decision-making, carbon pricing can help encourage changes in production and consumption patterns, thereby underpinning low-carbon growth [354]. Furthermore, by giving all emitters the same incentive to reduce their emissions, a pricing mechanism can cost-effectively reduce emissions [355].

There is a growing consensus among both governments and businesses on the fundamental role of carbon pricing in the transition to a decarbonized economy [355]. For governments, carbon pricing is one of the instruments of the climate policy package needed to reduce emissions. In most cases, it is also a source of revenue, which is particularly important in an economic environment of budgetary constraints. Businesses use internal carbon pricing to evaluate the impact of mandatory carbon prices on their operations and as a tool to identify potential climate risks and revenue opportunities. Finally, long-term investors use carbon pricing to analyze the potential impact of climate change policies on their investment portfolios, allowing them to reassess investment strategies and reallocate capital toward low-carbon or climate-resilient activities [356].

1) **Main types of carbon pricing** an emissions trading system (ETS) is a system where emitters can trade emission units to meet their emission targets. To comply with their emission targets at least cost, regulated entities can either implement internal abatement measures or acquire emission units in the carbon market, depending on the relative costs of these options. By creating supply and

demand for emissions units, an ETS establishes a market price for GHG emissions. The two main types of ETSs are cap-and-trade and baseline-and-credit [357]:

- Cap-and-trade system is a market-based environmental policy that places a limit on harmful pollutants and creates a market-based price on emissions. Companies need to hold permits to cover their emissions; these permits, often called "allowances," can be purchased or sold at prices determined by supply and demand [358]. The cap on GHG emissions generates a firm limit on what is permissible in any given region. This restriction strengthens over time, requiring agencies to continue making improvement toward better systems. It is a process that usually takes between 10 to 20 years to start reaching levels that are considered to be acceptable to the environment [359].
- Hybrid approaches – those that combine aspects of command-and-control and market-based incentive policies – are often discussed in the literature and increasingly used in practice. These approaches are appealing to policymakers because they often combine the certainty associated with a given emissions standard with the flexibility of allowing firms to pursue the least costly abatement method. However, hybrid approaches are not always the most economically efficient approach because either the level of abatement or the cost of the policy is greater than what would be achieved through the use of a market-based incentive approach [360].

2) **Carbon tax or emissions fee** is a fee that a government imposes on any company that burns fossil fuels. The purpose of a carbon tax is to expose the true cost of burning carbon. Those costs are experienced by those who bear the consequences, such as homeowners, farmers, and eventually the government. Carbon taxes make sure companies and consumers pay for the external costs they enforce on society [361].

3) **Cap and trade and carbon tax instruments** are market-based approaches that may be used to reduce GHG emissions. In many ways, a cap-and-trade program and carbon tax would produce similar effects. Both would place a market price on GHG emissions (directly or indirectly), and both would increase the relative market price of more carbon-intensive energy sources, particularly coal, which generate greater emissions per unit of energy. This result could lead to the displacement of these sources with lower carbon-intensive sources, including renewables; spur innovation in emission reduction technologies; and stimulate actions that may decrease emissions, such as efficiency improvements [362].

4) **An offset mechanism** designates the GHG emission reductions from project- or program-based activities, which can be sold either domestically or in other countries. Offset programs issue carbon credits according to an accounting protocol and have their own registry. These credits can be used to meet compliance under an international agreement, domestic policies or corporate citizenship objectives related to GHG mitigation [363].

5) **RBCF is a funding** approach where payments are made after pre-defined outputs or outcomes related to managing climate change, such as emission reductions, are delivered and verified. Many RBCF programs aim to purchase verified reductions in GHG emissions while at the same time reduce poverty, improve access to clean energy and offer health and community benefits [363].

6) **Internal carbon pricing** is a tool an organization uses internally to guide its decision-making process in relation to climate change impacts, risks and opportunities [363].

For governments, the choice of carbon pricing type is based on national circumstances and political realities (Fig. 55). In the context of mandatory carbon pricing initiatives, ETSs and carbon taxes are the most common types. The most suitable initiative type depends on the specific circumstances and context of a given jurisdiction, and the instrument’s policy objectives should be aligned with the broader national economic priorities and institutional capacities. ETSs and carbon taxes are increasingly being used in complementary ways, with features of both types often combined to form hybrid approaches to carbon pricing. Some initiatives also allow the use of credits from offset mechanisms as flexibility for compliance [362].

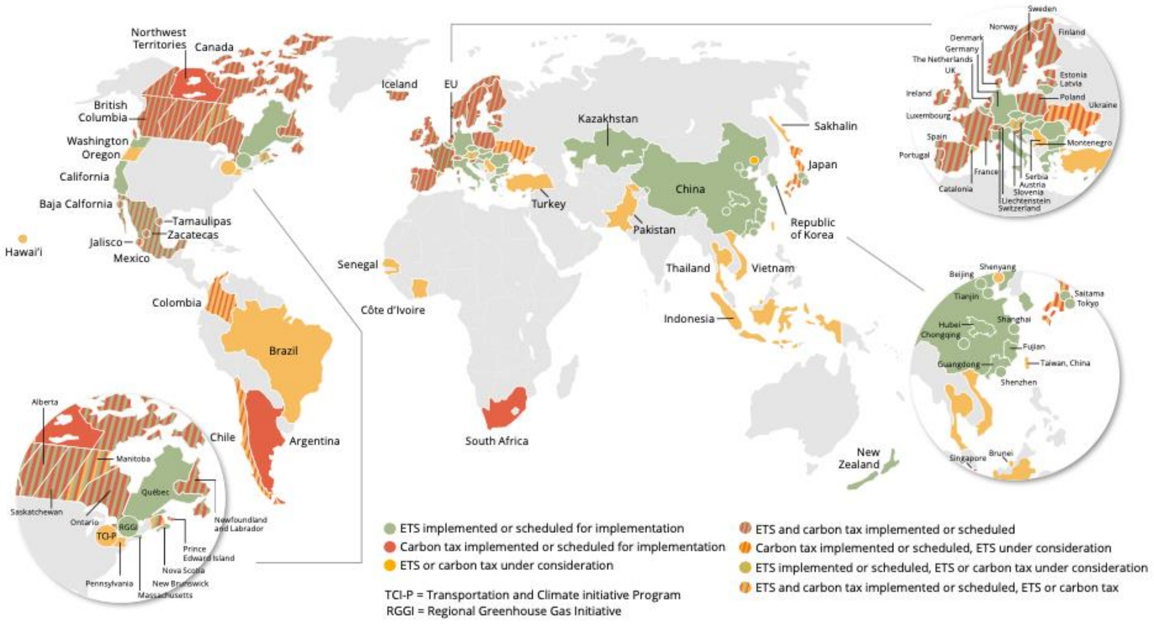


Fig. 54. Carbon Pricing Map [364]

The large circles represent cooperation initiatives on carbon pricing between subnational jurisdictions. The small circles represent carbon pricing initiatives in cities. In previous years, Australia was marked as having an ETS in operation. However, the Safeguard Mechanism functions like a baseline-and-offsets program, falling outside the scope of the definition of ETS used in this report. Therefore, the system was removed from the map. Rio de Janeiro and Sao Paolo were marked as considering the implementation of an ETS based on scoping work done in 2011 and 2012 respectively. Given there have been no updates since, the these were removed from the map.

Note: Carbon pricing initiatives are considered "scheduled for implementation" once they have been formally adopted through legislation and have an official, planned start date. Carbon pricing initiatives are considered "under consideration" if the government has announced its intention to work towards the implementation of a carbon pricing initiative and this has been formally confirmed by official government sources. The carbon pricing initiatives have been classified in ETSs and carbon taxes according to how they operate technically. ETS not only refers to cap-and-trade systems, but also baseline-and-credit systems as seen in British Columbia. The authors recognize that other classifications are possible.

Many companies utilize the carbon price they have in mandatory initiatives as a basis for their internal carbon price. Some companies adopt a range of carbon prices internally to take into account different prices across jurisdictions and/or to factor in future increases in mandatory carbon prices. GHG emissions can also be implicitly priced through other policy instruments such as the removal of fossil fuel subsidies, energy taxation, support for renewable energy, and energy efficiency certificate trading [362].

Understanding EU's ETS

The ETS is the EU's main carbon pricing tool and covers emissions from the power generation sector, industry and intra-European flights, amounting to about 40% of total EU emissions [365]. It is a cap-and-trade system. A quantity cap of allowances is set and distributed to participants, including through auctions. However, there the risk of carbon leakage, of firms moving their activities to countries with laxer climate rule to control costs, remains. Carbon leakage distorts the trading system and is counterproductive to the process of reducing emissions [366]. This risk can be avoided by giving some ETS allowances for free [367].

Also, the system is designed so that the quantity of allowances reduces in a steady and predictable manner (known as the linear reduction factor) [251]. Auction prices are determined by the quantity offered at any given time and the level of demand [368]. Since 2009, a combination of factors (economic crisis and high imports of international credits) has led to a surplus of allowances, which ultimately resulted in a prolonged period of lower carbon prices (from €20-€25/tonne of carbon dioxide from 2005 to 2008, to €10-€15 between 2009 and 2011, and €5-€10 between 2012 and 2018) [365].

A Market Stability Reserve [369] was introduced in 2019 as a long-term solution to address this excess-supply. The surplus of allowances is largely due to the economic crisis (which reduced emissions more than anticipated) and high imports of international credits. This has led to lower carbon prices and thus a weaker incentive to reduce emissions. In the short term, the surplus risks undermining the orderly functioning of the carbon market. In the longer term it could affect the ability of the ETS to meet more demanding emission reduction targets cost-effectively. Since the system started in 2019, the carbon price has risen to the current level of €50.14 as of June 4, 2021; however, it has gone as high as €56.35 on May 14, 2021 (Fig. 56) [370].

Fig. 55. Daily EU ETS carbon market price [370]

However, carbon prices will have to keep rising if they are to contribute materially to EU decarbonization. It is of course difficult to identify a ‘target’ price, but there have been attempts to identify the level of pricing that can cause behavioral change. The Stiglitz-Stern High-Level Commission on Carbon Prices [371], for example, concluded that the carbon price should be between \$40-\$80 in 2020 and then between \$50-\$100 in 2030 if it is to reduce emissions.

The current EU price thus remains too low to reduce emissions in a manner consistent with EU climate objectives. Therefore, this year will be decisive for Europe’s climate policy, with a wide range of new legislation promised to align current EU climate and energy policies with a new emissions reduction target [372]. The 2030 climate and energy framework also include EU-wide targets and policy objectives for the period from 2021 to 2030. The key targets for 2030 are: At least 40% cuts in greenhouse gas emissions (from 1990 levels); At least 32% share for renewable energy; At least 32.5% improvement in energy efficiency [373].

The announcement of the European Green Deal recovery package and new 2030 mitigation targets has triggered wide-ranging changes for the European Union ETS. In 2020, the European Green Deal was also announced, including a proposal for the European Climate Law legislating a 2050 climate neutrality objective and a 2030 Climate Target Plan to reduce net emissions by at least

55% by 2030. As part of this, there will be a revision of the EU ETS, with a proposal expected in June 2021 to align it with the more ambitious 2030 target. In addition to considering a more ambitious cap trajectory and reviewing the Market Stability Reserve (MSR), the EU is planning to extend the ETS to maritime transport, ensure the contribution of the aviation sector is in line with new objectives, and assess the possibility of also extending carbon pricing to the trans- port and buildings sectors with a view to harmonizing economic incentives to reduce emissions while also raising revenue for climate action and addressing social and distributional concerns [374].

National carbon pricing instruments were also launched in several European countries. Following its departure from the EU, the United Kingdom stopped participating in the EU ETS on January 1, 2021. On the same day, the U.K. ETS came into operation, closely resembling the design of Phase 4 of the EU ETS. Covering the power, industry, and domestic aviation sector, the cap will reduce emissions by 4.2 Mt annually and will be revised in 2024 in line with the country's 2050 net-zero trajectory. Germany's national fuel ETS also came into operation, covering all fuel emissions not regulated under the EU ETS — around 40% of national GHG emissions. The Netherlands Industry Carbon Tax Act (Wet CO_2-heffing industry) entered into force on January 1, 2021, with a rate of EUR 30 (USD) stayed around the auction floor price of USD 16.68. Though auctions were under subscribed in May and August 2020, stronger demand returned by November. In the Regional Greenhouse Gas Initiative (RGGI), prices also remained relatively stable. This provides a stark contrast to the 2007–2008 financial crisis and subsequent economic downturn, which led to sustained price depressions across multiple systems [374].

In 2021, the revised EU ETS Directive entered into force, outlining the policy framework for the fourth trading phase (2021–2030). Compared to the third phase, revisions in the fourth phase include: (i) strengthening the annual rate of the cap reduction from 1.74% to 2.2%; (ii) implementing the MSR (in operation since 2019); (iii) better targeting leakage and allocation rules; and (iv) establishing the Innovation Fund for innovative and breakthrough technologies and the Modernization Fund to help Member States modernize their power sector. The 2021 cap for the EU ETS is set at 1572 $MtCO_2e$ for stationary installations, while the cap for emissions from the domestic aviation sector is 38 $MtCO_2e$ [364].

Understanding Carbon Pricing in the U.S.

In the US there is no national carbon pricing system to lower global warming-causing emissions. The two basic proposed options are either a carbon tax or a cap-and-trade (or cap-and-dividend) system. In the United States, President Biden is exploring the idea of a border adjustment tax on countries that fail to meet their climate obligations [375], making the United States the only country without a national carbon price to be openly considering border adjustments.

In the US, where environmental justice concerns have gained increasing prominence, the Transportation and Climate Initiative Program's draft rules propose the creation of equity advisory bodies and annual reviews of the Program's equity impacts, as well as dedicating a share of revenues to ensuring overburdened and underserved communities benefit from the Program [376].

New trends boost ventures of successful deployment of CCUS. The United States leads the global deployment of carbon capture and storage (CCS) technologies. A progressive policy framework and sustained government support have launched the roll-out of the next generation of CCS facilities. With impacts of climate change becoming ever more devastating, and the need to eliminate emissions as soon as possible, these are welcome developments. However, reaching net-zero emissions climate goals will require a 100-fold scale-up of CCS facilities between now and 2040, demanding further supportive policies and mechanisms [7].

Most carbon pricing developments in the United States are taking place on the subnational level. These include California, Hawaii, Massachusetts, Oregon, Pennsylvania, the RGGI, the Transportation and Climate Initiative Program, and Washington [364].

California, changes to California's Cap-and-Trade Program that were required by Assembly Bill 398 (Chapter 135, Statutes of 2017) [377] took effect on January 1, 2021. The major changes to the program are (i) establishment of a price ceiling, (ii) changing from a three-tier allowance price containment reserve to a two-tier reserve below the price ceiling, and (iii) reductions in the use of offset credits, especially for those generated from projects that do not provide "direct environmental benefits in the state." Under the upcoming 2022 Scoping Plan update, the California Air Resources Board (CARB) will be assessing suite of climate policies to chart the course to achieving carbon neutrality by 2045. As part of this update, CARB may identify additional opportunities to further strengthen the Cap-and-Trade Program to ensure it continues its role to help the state meet its GHG reduction targets. In 2019, the U.S. Department of Justice challenged the constitutionality of California's market linkage with Québec based on alleged violations of constitutional precepts, the most important being the Foreign Affairs Doctrine. In a July 17, 2020, decision, the U.S. District Court for the Central District of California ruled in favor of California, which affirmed the constitutionality of the program's linkage with Québec.

Hawaii Climate change policies for Hawaii are being coordinated under the state's Climate Change Mitigation and Adaptation Commission as mandated by Act 32, Session Laws of Hawaii 2017. One option, among others, that is being considered is carbon pricing. Carbon tax bills have been introduced in the 2020 and 2021 sessions; however, they have not passed to date. The State Energy Office, a member of the Commission, released a carbon tax study [378] in February 2021. The report modeled different policy packages to assess impact on emissions and considered revenue recycling options to address the distributional impacts of a carbon price.

Massachusetts in 2020: Limits on Emissions from Electricity Generators system reduced the share of allowances distributed through free allocation from 75% to 50%. The remainder, after an adjustment to account for banked allowances, were distributed via auctions. The system will increase to full auctioning by 2021. In 2021, Massachusetts finalized a new climate program establishing climate targets for 2030. The Massachusetts ETS may be revised to align with these targets.

Oregon In line with the Executive Order on Climate Action (Executive Order 20-04), the Department of Environmental Quality of Oregon submitted a report in June 2020, both of which focused on program options to cap and reduce emissions. However, the details of the program have not yet been determined, and it is not clear whether the program will be a baseline-and-credit or a cap-and-trade system.

Pennsylvania's Department of Environmental Protection released an update of its earlier proposal in April 2020 for a power sector ETS covering CO_2 emissions. The proposed regulation is largely consistent with the system design features of the Regional Greenhouse Gas Initiative (RGGI) Model Rule. A final proposal is expected in 2021, with 2022 as the earliest start date for Pennsylvania's ETS to join RGGI. It is estimated that Pennsylvania's power sector will emit approximately 40% of emissions covered under RGGI when the state becomes a part of the program. Pennsylvania’s inclusion would significantly increase the size of RGGI’s carbon market.

Regional Greenhouse Gas Initiative Virginia began participating in RGGI as of January 1, 2021, after the final legislation for establishing an ETS and participating in RGGI was adopted in February 2020. On February 2, 2021, RGGI states [379] also announced a plan for a third program review.

In the first three months of 2021, legislators in the United States House of Representatives and the United States Senate introduced five bills that aim to accelerate the deployment of carbon capture and storage (CCS). This accomplishment is remarkable for several reasons: first, because of the depth and breadth of the policy provisions inherent in the bills; second, because all of the bills have bipartisan cosponsors; and third, because of the speed with which the bills were released. From a political standpoint, it is noteworthy that these bills were introduced at all. Fresh off the passage of the Energy Act of 2020, a giant bill that effectively triples Congress’ yearly authorized spending levels for CCS [380].

The new policy landscape with the new bills aimed at the long-term growth of CCS industry. Thus, CCS shows evidence that it might be the only major climate change technology that possesses such a robust level of support from Congress. The increase in both enacted and introduced CCS legislation over the past three years should encourage many more potential developers and investors to get serious about deploying CCS.

6.12.1. The Three Pillars of US CCS Policy

1) CCS policy measures implemented in the US can be grouped in one of three distinct categories: Research, Development and Demonstration (RD&D), 2) Market Development, 3) Infrastructure. It is best to think of these categories as pillars because they work in tandem to support wide scale CCS deployment; all three must be present in some form to fully secure the initiative [349].

2) CCS Research, Development and Demonstration (RD&D)

From bench-scale research to large-scale demonstration facilities, CCS-RD&D has historically been the first policy pillar to be constructed around the globe and has consequently provided the most robust support for advancing CCS technology. Many governments are currently funding CCS RD&D programs [381]

3) CCS Market Development

The 'Markets' pillar includes any policy that supports the business case for companies to invest in CCS facilities. Examples of policies that fall under this category are tax credits, carbon prices, carbon trading markets, regulations and standards that require a certain amount of 'low carbon' energy generation [349].

CCS Infrastructure

Infrastructure is the third pillar and encompasses policies that facilitate CO_2 transportation, utilization and underground storage. These measures frequently involve regulations, permitting, licensing and citing as well as the creation of common carrier pipelines or other policy trifecta is necessary to achieve the 100-foldincrease needed to meet climate scenarios laid out by the Intergovernmental Panel on Climate Change (IPCC) [328]. Individual facilities can and do exist apart from policy support, but in order to accelerate the deployment of CCS facilities and the growth of a truly global industry, all three policy pillars will need to be s significantly strengthened [349].

6.13.1. History of enacted CCS Policy in the U.S.

Since 1997 the US has implemented major CCS policies (Fig. 57)

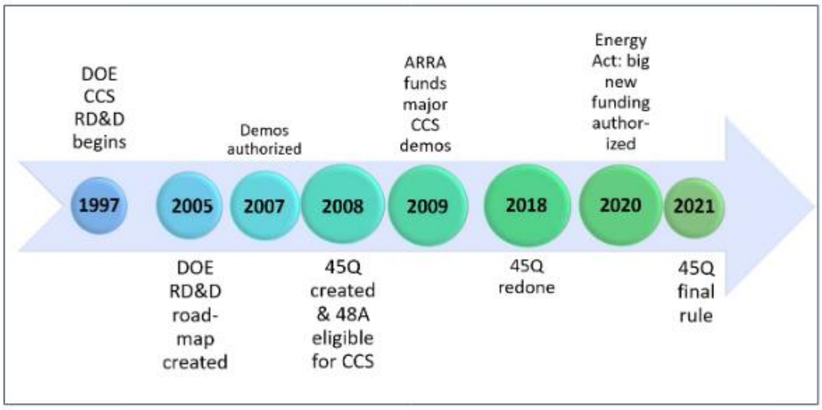


Fig. 56. Timeline of major CCS policy enacted in the US [349]

In 2021 the US finalized the 'Treasury Department and IRS 45Q Guidance' along with the five major CCS Bills.

The Final Guidance of 2021 was approved on January 6th, 2021. The Treasury Department and IRS issued their Final Guidance for the administration of the 45Q tax credit. This Guidance provides certainty for CCS project investors and developers by establishing transparency about how to build a CCS project to achieve the full value of the reformed 45Q tax credit in a timely manner [382].

6.13.2. Major CCS Bills Introduced in 2021

On 3 January 2021 the 117thCongress was sworn in. It includes the most closely divided House and Senate in decades. Yet, in the space of three months, this new Congress has introduced five major bipartisan bills to increase the deployment of CCS.

ACCESS 45Q Act –H.R. 1062

On 16 February, Representative David McKinley (R-WV) and original co-sponsor Rep. Marc Veasey(D-TX) introduced the ACCESS 45Q Act [382]. As its title suggests, the bill would amend 45Q to include a100% direct pay option (cash payments in lieu of the tax deduction), a 10-year extension (end of 2035) of the commence construction deadline (the date when a project must break ground) to qualify for the credit and would also allow 45Qthe same exception against the base erosion and anti-abuse tax (BEAT)as is enjoyed by wind and solar tax credits. (The BEAT is a form of alternative minimum tax for corporations to ensure multinationals cannot use deductions based off taxes paid abroad to reduce their US tax liabilities below a certain threshold.) Currently, the ACCESS 45Q Act has five Republican and five Democratic cosponsors [349].

1) Carbon Capture Modernization Act –S. 661, H.R. x

This bill, introduced on 10 March, amends the statutory language passed in 2005 and 2008 to allow coal-fired power generation carbon capture retrofits to profit from the 30% 48A tax credit. Specifically, the bill would relax the efficiency requirements for new and retro fit projects if they have CCS equipment on the thereby making it technically possible for a coal-fired power generation facility to deploy carbon capture technology and meet the efficiency requirements to qualify for the tax credit. In total, there is \$1.25 billion authorized for facilities that can invest in a CCS retrofit [383].

2) Storing CO_2 and Lowering Emissions (SCALE) Act –H.R. 8995

Introduced on 17 March, the SCALE Act [384] is the first major bipartisan bill introduced in both chambers of Congress to focus solely on the third policy pillar: CCS infrastructure. It builds on the INVEST CO_2 Act introduced by Rep. Cheri Bustos in 2019 [385] and authorizes \$4.9 billion in spending over 5 years. Major bill provisions include: 1) The establishment of the CO_2Infrastructure Finance and Innovation Act (CIFIA) program which would make flexible, low-interest loans for CO_2transport infrastructure projects available and provide grants for initial excess capacity on new infrastructure in order to incentivize building bigger pipelines; 2) The establishment of the Secure

Geologic Storage Infrastructure Development Program to make cost-sharing available for the development of large-scale saline geologic storage sites that can serve as hubs for multiple CCS facilities; 3) More funding for Environmental Protection Agency(EPA) Class VI permitting (the permit needed to do underground CO_2storage)in saline geologic formations and gives grants that benefits states establishing their own Class VI permitting programs; 4) Grants for states and municipalities to buy low and zero-carbon products made from $CO_2$and carbon oxides [349].

3) Carbon Capture, Utilization and Storage Tax Credit Amendments Act–S. x.

On 25 March, an evenly split bipartisan group of six Democrats and six Republicans introduced the Carbon Capture, Utilization and Storage Tax Credit Amendments Act [386]. It contains three provisions (with minor variations) found in the ACCESS 45Q Act. First, the bill extends the commence construction deadline for 45Q project eligibility but only for 5 years. (It's 10 years in ACCESS 45Q.) It also establishes a direct pay for both 45Q and 48A tax credits. Moreover, it allows 45Q the same exception against the BEAT tax as is enjoyed by wind and solar tax credits. Like the Carbon Capture Modernization Act, the Carbon Capture, Utilization and Storage Tax Credit Amendments Act would fix the 48A tax credit language to make coal-fired power retrofits eligible for a 30% investment tax credit. Finally, the Carbon Capture, Utilization and Storage Tax Credit Amendments Act increases the 45Q credit value from \$50 to \$120 per metric ton for direct air capture (DAC)facilities that capture and securely store carbon dioxide (CO_2) in saline geologic formations and from \$35 to \$75 per ton for DAC facilities that store captured CO_2 in oil and gas fields [349].

4) Financing Our Energy Future Act –S. x., H.R. x.

One day after the introduction of the Carbon Capture, Utilization and Storage Tax Credit Amendments Act,26 March, five Democratic and four Republican Senators introduced the Financing Our Energy Future Act, and a Democrat and Republican Representative released the same bill in the House [387]. The bill allows CCS projects to avail themselves of tax-advantaged master limited partnerships (MLPs). By doing this, it reduces the cost of equity and provides CCS developers with access to capital on better terms. MLPs are important tool for financing all types of CCS projects including DAC and also carbon utilization projects [349].

6.13.3. Linking EU and US Emission Trading System

A global carbon market is frequently called as the most cost-effective way to reach emission reduction goals [388]. The EU and the US are considered the two largest integrated economies in the world. A transatlantic link between EU's emissions trading system (ETS) and US's federal system would not only be a strong political indication for the formation of a global carbon market but would remove competitive concerns between these two key players triggered by different carbon prices [389]. If a combined EU-US market was established, this transatlantic market would provide the cornerstone for the overall international climate system, with subsequent expansions to other developed and developing countries [390].

Corporations are also exploring possibilities to source credits closer to where their clients are, for instance, in Western Europe and the United States. For some companies, in particular those serving consumer markets, the possibility to establish a clear correlation between their local environmental impact and crediting projects is attractive, and there is a willingness to pay a higher price than the average in the market. This is fostering a growing number of local standards covering emissions that are not tapped by other existing carbon pricing instruments. North America is purchasing most of its carbon credits in its region, with buyers in Oceania purchasing 41% of their credits locally. The share of local carbon credits bought by European buyers, in contrast, remains small. However, buyers' willingness to pay more than three times as much for these credits is leading to a growth in the number of local European standards, with four new standards having been launched in the past two years [364].

However, the environmental and economic benefits of emissions trading and by extension of linking crucially depend on the design of the trading systems. Particular areas of concern are the protection of the environmental integrity of the trading system as a whole, avoidance of negative economic or distributional impacts, and protection of design choices made in the establishment of an ETS [391]. Possible mechanisms for linking the EU to an US ETS could include direct and indirect, bilateral and unilateral links, as well as various possible legal mechanisms to implement the link, such as treaties or more informal agreements [392].

Linking means that one system's trading units can be used, directly or indirectly, by a participant in another system for compliance. The inclusion of more participants entails a greater diversity of sources and more abatement options. This should in turn lead to improved market liquidity and result in a more efficient allocation of resources towards least-cost abatement measures and thus lead to lower overall compliance costs [393] [394]. As an additional benefit, linked trading schemes with harmonized prices eliminate any competitive distortions that might arise from different pre-link carbon prices between linking partners. Linking the emerging domestic systems could also be politically significant since they would serve to underpin the top-down approach of the international climate regime by a bottom-up process which might further strengthen the international regime via bi- and plurilateral agreements [395] [396].

Nevertheless, these possible advantages are based on a best-case scenario where countries establish environmentally effective emissions trading systems and then link them with each other [397]. Real-life emissions trading systems will not necessarily be environmentally effective. The environmental benefits of emissions trading and, by extension, of linked trading schemes are highly dependent on the design of a trading system. Most importantly, the amount of emission reductions achieved by cap-and-trade stems not from the trading as such, but from the stringency of the cap [398].

The environmental effectiveness of emissions trading is also determined by whether cost-containment features such as price caps are used. Through linking, such features would impact the combined trading scheme and thus impair rather than enhance its environmental effectiveness [399]. It is therefore not advisable to link emissions trading systems without any regard to their design. To the contrary, key features that determine the environmental effectiveness of trading schemes, such as the cap and cost-containment features, should be harmonized prior to linking [400] [399].

The economic and technical side of ETS linking political drivers and barriers have so far been underrepresented. There have been some attempts in employing the concept of linking activities of the EU: (1) a failed linking attempt: EU ETS–California Cap-and-Trade Program [401]; (2) a successful linking treaty: EU ETS–Switzerland Emissions Trading System; and (3) an agreed-upon but not realized link: EU ETS–Australia Carbon Pricing Mechanism [402].

7. Conclusions

The main subject of this work revolves around the CO_2 molecule, a low-value, low-energy, stable waste gas, often available in large quantity in single locations. This work examines some viable avenues to capture, utilize, and store CO_2 (CCUS)- with the ultimate goal of reducing GHGs emissions and global warming. Moreover, the study also examines various paths to accelerate the commercialization of the carbon-based products and their technologies.

New CO_2 use pathways, involving chemical and biological technologies, offer opportunities for future CO_2 use. Many of these pathways are still in an early stage of development, but early opportunities are already being realized. When comparing the technologies utilized to create the two carbon-based products (synthetic fuels and carbonates) and biogas to produce electricity, it was observed that when fly ash reacts with CO_2 through the process of mineral carbonation, it converts carbon into a thermodynamically stable and insoluble solid that can store CO_2 for long periods of time. Carbonated products are considered a permanent CO_2 storage solution; conversely, synthetic liquids are a reuse technology which do not permanently store CO_2, hence, CO_2 is converted into a less stable product. Additionally, the conversion of CO_2 into syngas is even less stable since the final product is a gas, making it the least ideal product to store CO_2.

Carbon dioxide can be captured from gaseous waste streams containing CO_2 by using technologies that are commercially accessible and by the implementation of established chemical processes.

Currently CCU technologies are experiencing various stages of performance and maturity; nonetheless, there are significant advancements in CCU technologies that have progressed in the past ten years; various technologies showing promising commercial scalability and advanced mobility features. Furthermore, the swift decline of costs for many renewable sources (mainly solar and wind) has made low-cost, near-zero-carbon electricity abundant in terms of capacity and locality. Consequently, this has driven some markets to offer electricity at affordable cost and, in some cases even negative prices. Because renewable electricity is gradually decreasing in price, there has been an increase cognizance on prospective new applications, (e.g., CCU and CCUS) considering turning this trend into a profitable venture.

The reality of CCU/CCUS is multifaceted and complicated. It embraces an extensive assortment of applications (e.g., synthetic fuels from CO_2 conversion using electrolysis of water and carbonated fly ash for the cement and concrete industry), technologies (e.g., electrochemical conversion using fuel cells, thermo-catalytic conversion to produce polymers, mineral carbonation) energy necessities (i.e., exothermic vs. highly endothermic), and locales (i.e., sizable industrial sets vs. distributed applications). Consequently, the ultimate value and extent of carbon utilization will depend on future technology, economics, and policy drivers.

The long-term mitigation impact of carbon utilization technologies will depend on the life-cycle emissions from production through the end use of the product. Important aspects defining the mitigation potential of carbon utilization technologies and resulting products include the GHGs emissions associated with the product production, the volume of carbon embedded in the product (depending on the size of the product market and amount of carbon incorporated), the product lifetime during use, and ultimately the carbon captured in the product at end of use. Different products and processes will have different resulting mitigation impacts, and carbon waste stream utilization may be pursued for reasons other than long-term carbon mitigation.

Decisions about whether to commercialize a product are complex. It is necessary to establish proof of value, that is, to determine if the technology either addresses a limitation of the current market (such as by lowering the cost or increasing the lifespan of a product) or fills a new need in the market. Issues associated with capital expenditure, regulations, and availability of feedstocks are all crucial and may vary depending on the location in which a new technology is being implemented. Commercialization considerations are also time dependent; a technology that is not commercially viable today may become so in the future because of market, policy, or societal changes. Similarly, regional factors may dictate commercial viability such that technologies that are commercially viable in one region may not be feasible elsewhere. Because carbon utilization involves goals related to the mitigation of greenhouse gas emissions, environmental considerations are also important for evaluating these technologies [403]

When evaluating the three carbon capture technologies and their products the following factors were observed.

Biogas production to generate electricity and heat by using fuel cells:

The allure of introducing solid oxide fuel cells into the WWTP market goes beyond the advantage of fuel flexibility. While traditional cogeneration systems produce exhaust gases with CO_2 mixed with a high nitrogen flow, with related difficulties in the sequestration processes, in a SOFC systems exhausts from the anode side are free from nitrogen, leading an easy CO_2-capture through a simple condenser to remove water. However, the main criticality related to biogas use in SOFC is the need for a biogas cleaning system, which is a non-standard component required when biogas is fed to SOFC. Compared to traditional CHP system, SOFC are more sensitive to biogas contaminants such as Sulphur and siloxanes. Fortunately, biogas resulting from WWTP shows relative low levels of contaminants further contributing to the attractiveness of WWTP as a market opportunity to implement SOFC. Because of a relative ‘clean’ biogas, SOFC installations in WWTP usually required only a single stage contaminants removal, by using adsorption materials.

Production of synthetic fuel- methane and methanol

Two different plants are to produce synthetic fuels from hydrogen and carbon dioxide have been assessed from a technical and economic outlook. A variation cost of both products (methane and methanol, respectively) as a function of the electricity cost for a specific SOEC cost equal to 1,050 \$/kW, parametrized with the cost of CO_2 as a market commodity. The distance between the two lines is greater in the case of a methanol synthesis plant, due to the higher amount of CO_2 required from the stoichiometry of the methanol formation reaction (Fig. 39).

Reviewing the methane production plant, the abundant exothermicity of the reaction allows for an exceptional thermal integration between the fuel synthesis and the steam generation, minimizing and making almost zero the external heat requirement. The strong thermal integration, combined with the high conversion reached within the catalytic reactors, leads to high conversion efficiency (≈ 77%). On the other hand, for the methanol production a higher reaction pressure is required. Therefore, if the higher reaction pressure is combined with the minimal heat available from the reactor, the efficiency of the system is diminished (≈ 58%) because of the larger demand for external energy. The need of higher pressure for methanol production means that the initial investment and O&M costs are greater.

With fixed electrolysis size (10 MW) the carbon dioxide utilization for the methanol synthesis case is higher than the CO_2 consumed for methane production (1,594 kg/h vs. 2,751 kg/h), due to the stoichiometry of the involved chemical reactions.

When evaluating a sensitivity analysis, it was visible that the two considered systems present similar economic performance, unlike the difference between the efficiency of the two analyzed concepts. With current (2,500 \$/kW) SOEC specific cost the breakeven electricity price (enabling the production cost comparable with the upper fossil-based bound) is very low: it equals 3 and 20 \$/MWh for synthetic methanol and methane, respectively. The electrolysis section cost decrease allows a wider spectrum of acceptable electricity prices: e.g., below 40 and 60 \$/MWh for synthetic CH_3OH and CH_4, respectively, in the most optimistic SOEC cost assumption (450 \$/kW). In the scenario assuming no cost for input electricity (situation occurring more and more in different developed countries), the capacity (or utilization) factor ensuring the competitiveness of power-to-fuel system is in the range between 20-50% (synthetic methane) or 30-60% (synthetic methanol).

It was concluded that, to produce an economically attractive market for e-methane and e-methanol, in the present market conditions, the production plants should maintain a utilization factor of approximately 50%, the cost of SOECs should be near to 1050 €/kW and the electricity required to run the system needs to be supplied from renewable sources at a very low cost (below 40-50 $/MWh).

Production of carbonated fly ash

The progress of commercially feasible carbonation technologies is affected by gaps in our understanding of carbonation processes, technical challenges fronting various carbonation approaches, and an array of economic and social factors affecting the possible costs and market penetration of mineral carbonation technologies. Furthermore, the potential influence of these measures to climate change is prone to be limited as demand for these products becomes saturated. Also, the regulations and standards- mainly, the study of codes and specification framework are usually overseen by members of government and industry. Additionally, the hurdle to accelerate the route to make any changes to the regulatory framework so to not discourage investors can consequentially hinder the entrance of a new technology into the market.

Given the very large material movements in the construction sector, this industry offers an incredible potential for CO_2 utilization. However, simulating and integrating CO_2 from extensively distributed sources with a variety of potential consumers and construction product types and markets poses logistical and commercial challenges. Additionally, research is needed to develop predictive accelerated aging evaluation methodologies for mineral carbonation. These models would help minimize the risk of new technologies and simplify their introduction into conservative market applications where extensive performance data are necessary to institute codes for use.

The specifications for the utilization of fly ash (EN 450-1) in the production of concrete are very restrictive, especially for Type C or HCFS ashes. In fact, there are no general existing regulation on the European level for using this by-product in the construction industry. In contrast, the American specifications related to fly ash and HCFA are somewhat vague and they have several loopholes that are being misused in when fly ashes are used in some projects. The is an immediate need to do more testing and research to be able to revise the current specifications- mainly ASTM C618.

In Europe there is a large production of HCFA due to the sizable amount of lignite burnt at coal power plants. Carbonation as a HCFA pre-treatment will make this material compatible with cement materials. Mineral carbonation technology would permit to bind the surplus of the free calcium in HCFA with anthropogenic CO_2. This process will change some of the chemical and physical properties of the fly ash and therefore enabling the use of the by-product to more applications. Moreover, by introducing the MC technology at thermal and municipal plants will help mitigate the emission of CO_2.

After further developing the MC process there needs to be more advanced research to study the durability and strength of cement-based products that include HCFA. This will result in the development of other technologies, the use of the product in more applications, the advancement of deploying large scale projects- ultimately facilitating and accelerating the commercialization of the technology and the carbon-base product.

Final Remarks

Determining the commercialization potential of a new product or process needs consideration of factors beyond the technology and economic feasibility, for example, market-focused and legal mechanisms. Market-focused entails an evaluation of the end market size, competitiveness and perception of the technology in question; while legal components include consideration of regulatory matters, intellectual property, and standards and norms in the market of interest.

Carbon Capture is a high-cost abatement option and will remain so in the short-term and, unlike renewable energy and energy efficiency, it does not generate revenues if there is no carbon price or a commercial market for the captured CO_2. Current carbon prices (around 50 €/tonCO_2 according to the ETS system) are well below carbon capture costs because current short-term emissions targets can be met without the use of capturing systems.

Moving away from conventional processes and products will require a number of developments such as: (i) education of producers and consumers; (ii) new standards; (iii) prevailing research and development to address the issues and barriers challenging emerging technologies; (iv) government funding for development and deployment of emerging technologies; (v) rules and regulations to address the intellectual property problems related to the diffusion of new technologies; and (vi) financial incentives (e.g., through carbon trading mechanisms) to make emerging low-carbon technologies, which may have a higher initial costs, competitive with the conventional processes and products.

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